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Characterization of Boliden's Sulfide Lime Precipitation Plant

Kentucky Univ.
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Excellent removal of most metals, including arsenic was shown. Process control problems precented 99%+ removal of all metals however. (Questions etc.)

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CHARACTERIZATION OF BOLIDEN'S SULFIDE - LIME PRECIPITATION PLANT

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report provides information on the soluble sulfide precipitation process (Na_2S) used at a copper/lead smelter for treatment of wastewater. The study presents the results of a sampling study which aimed to define the process kinetics of a full scale plant. The generation of H_2S gas, metals removal, and sludge handling are discussed. For more information contact the Nonferrous Metals and Minerals Branch.

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Cincinnati

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SUMMARY OF RESULTS

Boliden Metall Aktiebolag uses a sulfide precipitation process for the removal of heavy metals from the aqueous effluents from their copper-lead smelter in Skelleftehamn, Sweden. They subsequently precipitate fluorides from these waters by calcium hydroxide addition. The efficiencies of these two processes in removing heavy metals and fluorides were measured in January and February, 1979, by Boliden and Radian personnel. The following results were found:

1) The removal efficiencies for As, Cu, Pb, Cd, Zn, Hg, and F for the combined sulfide-lime precipitation process were excellent, as shown in Table 1.

2) Arsenic and zinc removal by the sulfide process alone was not always satisfactory because of As/Zn interaction.

3) pH control only was found to be insufficient for simultaneous arsenic and zinc removal at optimal efficiency.

4) Excess sulfide addition causes no odor problem. Sulfide is apparently consumed through reaction with sulfite (liquid-phase Claus reaction) in the waters.

5) The following elements were analyzed for in the combined process outlet waters by using a semi-quantitative inductively coupled plasma emission spectroscopy method:

Ag	Be	Cr	Mn	Pt	Sr	W
Al	Bi	Cu	Mo	Sb	Sr	Zn
As	Ca	Fe	Na	Se	Ti	Zr
Au	Cd	K	Ni	Si	U	
B	Co	Mg	Pb	Sn	V	

All heavy metals with the exception of As were found to be reduced to less than 1 ppm.

TABLE 1. ELEMENT REMOVAL IN THE SULFIDE AND COMBINED SULFIDE-LIME TREATMENT PROCESS*

Element	Inlet mg/ℓ	Outlet Sulfide Process Only mg/ℓ	Outlet Sulfide & Line Processes Combined mg/ℓ	Removal
Arsenic	442	146	19.1	96%
	122	16.0	1.8	99%
	170	37.8	1.9	99%
	150	33.1	4.1	97%
	131	24.2	1.9	99%
Copper	0.9	<0.1	<0.1	>90%
	0.4	0.1	0.1	75%
	1.2	0.1	0.1	92%
	0.4	0.1	0.1	75%
	0.1	0.1	0.1	--
Lead	7.1	0.2	0.2	97%
	4.5	0.1	0.1	98%
	5.9	0.2	0.2	97%
	8.6	0.2	0.1	99%
	7.8	0.2	0.2	97%
Cadmium	2.85	0.05	0.05	98%
	5.7	0.01	0.01	99%
	3.6	0.01	0.01	99%
	4.4	0.01	0.01	99%
	14.8	0.12	0.01	99%
Zinc	36.2	39.0	0.5	99%
	52.2	16.4	0.1	99%
	45.1	22.0	0.3	99%
	33	15.0	0.1	99%
	55	13.6	0.1	99%
Mercury	1.2	0.011	0.011	99%
	0.9	0.016	0.012	99%
	0.9	0.012	0.008	99%
	1.3	0.044	0.01	99%
	0.8	0.068	0.012	99%
Fluoride	89.6	89.7	34.4	62%
	100	82.3	20.8	75%
	117	120	26	78%
	124	103	32.9	68%
	110	86	26.2	70%

* Total Metals

6) Analyses for organic criteria pollutants showed negligible levels in both inlet and outlet waters.

7) Vacuum filtration of the thickener underflow from the process indicated that metal sulfide sludge (for possible metal recovery) containing 20 to 25 weight percent solids could be obtained.

Process optimization could be improved by studying the precipitation kinetics of As_2S , CuS, and ZnS. Consumption of sulfide through reaction with SO_2 needs to be minimized. In addition, a more sophisticated sulfide addition control strategy must be developed.

SECTION 1

INTRODUCTION

Boliden Metall Aktiebolag operates a copper and lead smelter at its Ronnskar Works in Skelleftehamn, Sweden. Boliden has installed scrubbers to capture dust, HCl, and HF in various smelter off-gases and equipment to produce sulfuric acid and liquid sulfur dioxide. The blowdown streams from these gas scrubbers are highly acidic and contain heavy metals. Rain and wash waters from throughout the smelter comprise another source of heavy metal contaminated wastewaters.

Swedish effluent regulations required the removal of heavy elements before wastewaters are discharged. In response to these regulations, Boliden compared hydroxide and sulfide precipitation processes for removal of heavy metals from these waters at the bench scale. On the basis of these laboratory data, they decided to remove these heavy metals by a combined sodium hydroxide-sodium sulfide precipitation process. Fluoride discharge is controlled in a separate step by precipitation with calcium hydroxide. The heavy metal sulfide precipitates are recycled, while the calcium fluoride precipitate is discharged.

A full-scale sulfide-lime precipitation plant started up in May, 1978. The addition of the NaOH and Na_2S reagents has been regulated by monitoring pH. A large increase in the quantity of water to be treated and a much higher than expected arsenic level has caused complications during the first year of operation.

In a joint effort, Boliden and Radian characterized the plant performance in January and February, 1979. A test plan was devised to determine the heavy metal removal of the overall process in three short tests (ST-01, ST-02, ST-03), and to determine the performance of the individual process vessels in two more detailed or "long" tests (LT-01 and LT-02). Difficulties in closing a sulfur balance around the process prompted the execution of two special short tests (SST-01 and SST-02).

The following chapters describe the details of the characterization effort. In Section 2, the process is described and a survey of the plant operating history is given. Section 3 describes the test program design and the analytical methods employed. Finally, the results of the test program are presented and discussed in Section 4.

SECTION 2

PLANT DESCRIPTION

Process Description

Boliden's sulfide precipitation process was developed to clean smelter wastewaters contaminated with heavy metals. The process accomplishes three goals.

- Heavy metals are precipitated as metal sulfides which can be recycled to the smelter.
- Acids are neutralized.
- Fluoride is removed in a separate step for disposal.

The waters treated in the sulfide precipitation plant consist of scrubber blowdown, plant wash water, and rain water. These waters contain heavy metals and are normally acidic. The major constituents are arsenic (500 mg/ℓ) and zinc (100 mg/ℓ). Copper, lead, bismuth, antimony, mercury, and selenium are present in smaller amounts (a total of 40 mg/ℓ).

The incoming water is first partly neutralized, then sodium sulfide is added. The amount of reagent added is controlled by monitoring the pH, i.e., the addition of sodium sulfide is stopped when a predetermined pH value is reached.

The design flow rates are 100 m^3/h for rain and wash water and 75 m^3/h for process water, with a maximum combined flow rate of 175 m^3/h. The pumps feeding the first reaction tank have two speeds; this allows the feed rates to be varied between 35 and 175 m^3/h. A schematic flow diagram of the process is shown in Figure 1. Vessel sizes are given in Table 2.

The two types of raw water, namely the process water and the rain and wash water are fed to two respective surge tanks in order to dampen the flow to the treatment plant. Because the incoming water, especially the process water, is normally very acidic, the pH is monitored continuously. The starting pH for sulfide addition is adjusted with sodium hydroxide. The concentration of the sodium hydroxide solution used is 40 percent.

Sodium sulfide is added as a 15 percent solution to the first reaction tank, which has a 55 m^3 capacity. This results in a wastewater residence time of between 20 and 30 minutes at flow rates of 110 to 170 m^3/h.

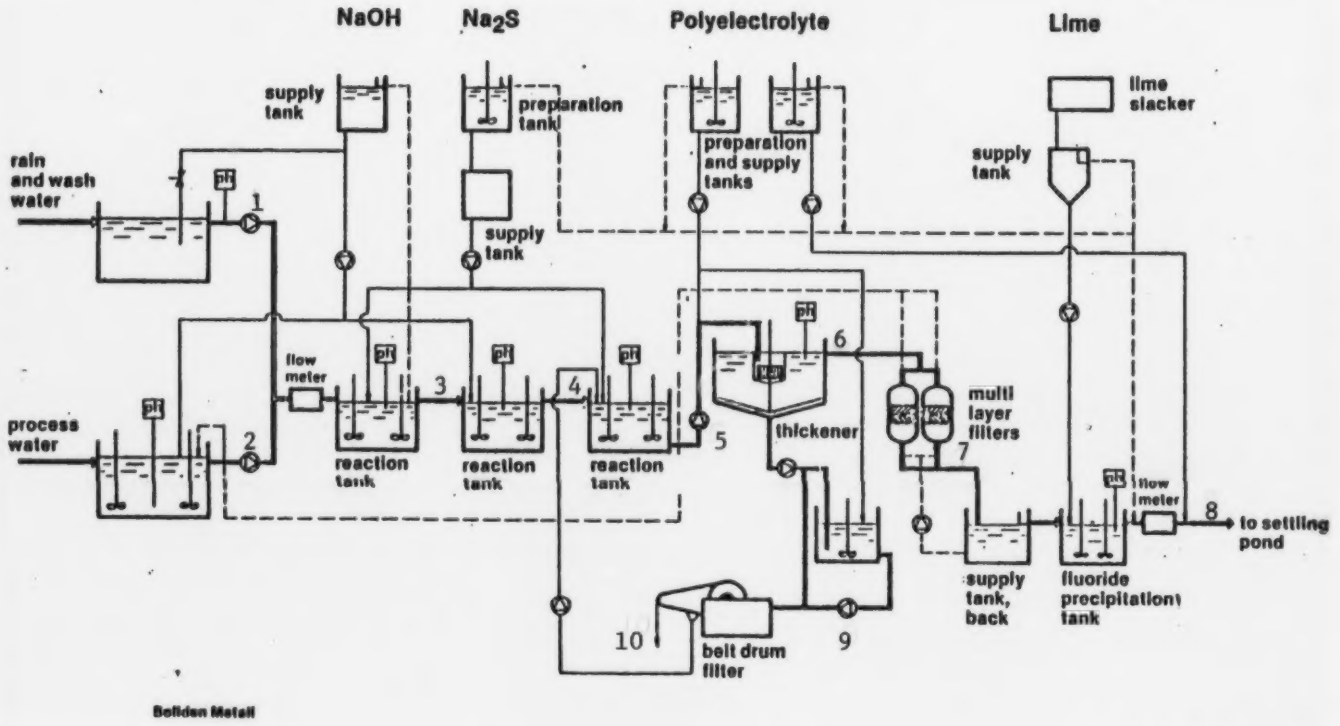


Figure 1. Sulfide precipitation plant.

TABLE 2. VOLUMES AND DIMENSIONS OF PROCESS VESSELS

Surge tank rain and wash water		180	m^3
Surge tank process water		140	m^3
Reaction tank 1		55	m^3
Reaction tank 2		36	m^3
Reaction tank 3		50	m^3
Thickener width		15	m
depth		3.5	m
volume		620	m^3
Multilayer filter width		3	m
depth:	anthracite sand	0.43	m
	garnet sand	0.33	m
	bearing material	0.23	m
Calcium fluoride precipitation tank		124	m^3
Sludge tank		45	m^3
Size of drum filter		47	m^2
Size of lime slaker		900	kg/h

The third reaction tank is also equipped to allow the addition of more sulfide. This is sometimes necessary in order to compensate for secondary reactions.

The wastewater-precipitate slurry is pumped from the third reaction tank to a thickener where flocculant is added to enhance sedimentation properties. The sludge from the thickener underflow is further concentrated by using a belt drum filter. The filtrate is returned to the reaction tanks. The overflow from the thickener is polished in one of two parallel multilayer filters.

The effluent from the polishing step is fed to the fluoride treatment plant. A 10 percent lime slurry is added to adjust the pH to 10 or greater. The residence time in the CaF_2 precipitation tank is 45 to 60 minutes. The CaF_2 slurry is pumped to a settling pond. The overflow from this settling pond is fed to an intermediate holding pond for discharge to the smelter effluent receiver.

The addition of all the chemicals - sodium hydroxide, sodium sulfide, and lime-is controlled by means of pH. The pH levels were controlled by manual set points until June, 1979. At that time, a microprocessor was installed.

The 15 percent Na_2S solution and the 10 percent lime slurry are prepared within the plant. The 40 percent sodium hydroxide solution is purchased commercially. The mixing tanks are instrumented with level controls. Occasional overflows from these mix tanks are directed to the exit stream of the CaF_2 precipitation tank.

Operating History

Start-up of the plant was in May, 1978. During the first month, only process water was treated, then rain and wash water were added. Plant availability during the first year was less than 100 percent. Difficulties encountered were:

- Equipment malfunctions,
- Instability and short lifetimes of pH sensors,
- Divergence between plant design parameters and actual conditions.

Equipment malfunctions have not yet been completely eliminated after one year of operation. The most serious problem was created by the speed and size of the impellers in the reaction tanks. Incomplete mixing causes unsatisfactory precipitation.

The process is controlled primarily by pH meters. Instability and short lifetimes of pH probes were observed due to attack by fluorides in the acidic solution. Clogging of pH meter sampling lines also occurred.

The biggest setback to plant operation was the great difference between the design parameters and the conditions actually encountered. Not only did the wash and rain water prove to be very contaminated, but the flows were higher than expected. In addition, the arsenic concentrations were occasionally 10 times higher than those assumed during process development and design.

Several corrective steps have been taken. An effort was made to minimize wash water flow through an educational campaign throughout the plant, i.e., people were made aware of the necessity of shutting off the taps as soon as washing was over. Also the sources of arsenic were identified and characterized. Efforts are being made to treat waters which were found to be high in arsenic, but low in concentrations of other heavy elements in an existing special arsenic removal plant rather than discharging these waters to the sulfide precipitation plant. Economic as well as technical considerations favor arsenic removal by lime precipitation rather than by the sulfide process. In addition, lab work was started to find the best modification of the sulfide precipitation method for treatment of combined waters high in arsenic concentrations.

On the other hand, some process steps have worked better than anticipated, for example, the filtering of the sludge. The filtering capacity of the drum filter exceeded the design specifications of 4 kg dry sludge/m^2h even without the addition of polyelectrolyte. However, during the test period discussed in this report, Boliden was evaluating a new polyelectrolyte, which was subsequently found to result in poor sludge handling properties. Since this test period, Boliden has returned to the use of a more effective polyelectrolyte, and again has experienced no problems with the filtering of the sludge.

The calcium fluoride precipitation step worked as anticipated. The only problem is that arsenic and zinc not removed in the sulfide precipitation plant are precipitated with the fluoride. Zinc is precipitated as zinc hydroxide and arsenic as calcium arsenite.

The original precipitation conditions, namely pH adjustment to 4-5 with sodium hydroxide followed by Na_2S addition up to a pH rise of one unit, had to be abandoned. This approach gave unsatisfactory results in the presence of high arsenic concentrations. The plant is now operating as follows: The pH of the incoming waters is adjusted to 2.2-2.5. Next, sodium sulfide is added until a pH of 4 to 4.3 is reached. Sulfide sludge is then removed, and lime is added to precipitate CaF_2. The fluoride plant operates at pH 10 or greater.

The high fluctuations in the concentration levels pose control problems. Satisfactory removal of arsenic is achieved in the low pH range, while satisfactory removal of zinc is obtained at a higher pH range. Optimization of the process control is a prerequisite to achieving optimal removal. This necessitates the measurement not only of pH, but also of other parameters. For example, continuous monitoring of arsenic concentrations would be helpful.

SECTION 3

TEST PROGRAM

In this section, the methodology used to characterize the efficiency of Boliden's sulfide precipitation process is described. Both the sampling and analytical methods used are discussed here.

Sampling

Eleven sampling points were selected. They are shown in Figure 1. They were:

Point 1: Incoming rain and wash water
Point 2: Incoming process water
Point 3: Overflow from reaction tank 1
Point 4: Overflow from reaction tank 2
Point 5: Overflow from reaction tank 3
Point 6: Thickener overflow
Point 7: Multilayer filter effluent
Point 8: Overflow from CaF_2 precipitation tank
Point 9: Sludge from thickener
Point 10: Filtered sludge
Point 11: Effluent from CaF_2 pond

Three short tests, coded ST-01, ST-02, and ST-03 were performed. The goal of these tests was the determination of the overall removal efficiency for heavy metals. Only the incoming streams (Points 1 and 2) and the outgoing streams (Points 7, 8, and 11) were sampled.

All eleven points were sampled in two long tests, coded LT-01 and LT-02. The purpose of the long tests was not only to determine the heavy metal removal efficiencies of the whole system but also to follow the reactions in individual pieces of equipment. It was also hoped that these two long tests would provide sufficient information to calculate a material balance for the wastewater plant.

Several results of these tests pointed to an interaction of H_2S and SO_2. Therefore, special short tests coded SST-01 and SST-02 were performed to measure the extent of these interactions, which are also known as liquid-phase Claus reactions.

The flow rate and composition of incoming streams vary greatly in normal plant operation. Thus, no deliberate attempts were necessary to vary operating conditions during these tests.

Sampling Frequencies

Each test run went on for approximately 6 hours, except for the special short test where only one grab sample from each sampling point was taken.

Points 1 to 5 cover in principle the sulfide precipitation process. The points are placed at the inlet and outlet streams to the sulfide precipitation step. At these points, a sampling frequency of one sample every half hour for six hours was chosen. Half an hour was chosen as a reasonable sampling interval with respect to the changes of flow and composition of incoming streams and the residence time in the surge and reaction tanks. The process water flow varies between 35 to 75 m^3/h, and the surge for process water is 140 m^3. The surge tank for rain and wash water is 180 m^3, and the flow varies between 70 to 100 m^3/h. The residence time in the three reaction tanks varies between 15 to 30 minutes.

Samples were collected at Points 6, 7, 8 and 9 (thickener overflow, multilayer filter effluent, effluent from calcium-fluoride precipitation tank and thickener underflow) after the 3rd and 6th hour of the test run. The volume of the thickener is 620 m^3, and the residence time is 4-6 hours. Any fluctuations in the incoming stream composition are dampened in the thickener.

The calcium-fluoride precipitation step was also included to get a complete characterization of the existing plant. A low sampling frequency was chosen because of the dampening effect of the thickener, upstream.

Once, at the end of the run, samples from Point 10 (filtered sludge from the drum filter, if operating) and Point 11 (pond) were also taken. More frequent sampling was not necessary since the residence times in the sludge handling equipment and the pond are long. The sample frequencies and volumes are summarized below:

Sample Point	Sample Frequency	Size of Sample
1 to 5	Every ½ hour for 6 hours	0.5 liter
6 to 9	After the 3rd and the 6th hours	3 liters
10 and 11	One sample at the end of the run	0.5 and 5 liters

Samples of the reagents used by the process (sodium hydroxide, sodium sulfide, and lime) were taken once per test, and the concentrations of NaOH, Na_2S, and $Ca(OH)_2$ were determined.

Sample Handling

Figures 2 through 6 show sampling procedure flow sheets.

The pH and temperature of samples from Points 1 through 5 tests, and samples from Points 1 and 2 in the short test were measured immediately. In the beginning, the intention was to measure the sulfide concentration at these points at the same time by using a sulfide ion selective electrode. However, this had to be abandoned due to stability problems.

For each test run, a composite was made from all samples taken at Points 1, 2, 6, 7, 8 and from the pond effluents. The composites were taken to Boliden's smelter laboratory and filtered immediately after the test was over. Each filtrate was then divided into two parts. One was acidified with 10 N HNO_3 for the analysis of heavy metals, sodium, calcium, magnesium and sulfate. The other was used for the analysis of total sulfur, chloride, fluoride and total dissolved solids (TDS). Radian also analyzed samples of the acidified solutions by inductively coupled plasma emission spectroscopy.

Samples from Points 3, 4, and 5 (outlet of reaction tanks 1, 2, and 3) were expected to be unstable with respect to solid-liquid equilibrium. Three samples were taken at each point (3, 4, and 5) every one-half hour. One sample was used for analyses less sensitive to storage, i.e., analysis of solids content and determination of the soluble species of sodium, chloride, fluoride, magnesia, sulfate and TDS in the solution. A composite was made of these samples for each point, which was filtered afterwards. The second sample used for heavy metal and calcium analyses was immediately filtered and acidified with 10N HNO_3 on-site to avoid further precipitation in the solution and to prevent wall adsorption. The third sample was also filtered on-site. However, since this sample was taken explicitly for a sulfide determination, gravity rather than vacuum filtration was employed and the sample was not acidified, to avoid sulfide loss.

Analytical Methods

Heavy Metals

Most of the quantitative determinations of the cations were based on atomic absorption spectrophotometry. The solutions were aspirated directly into the flame after proper dilution.

Concentrations of the following elements were determined in this way:

arsenic	cadmium	sodium
copper	zinc	calcium
lead	iron	magnesium.

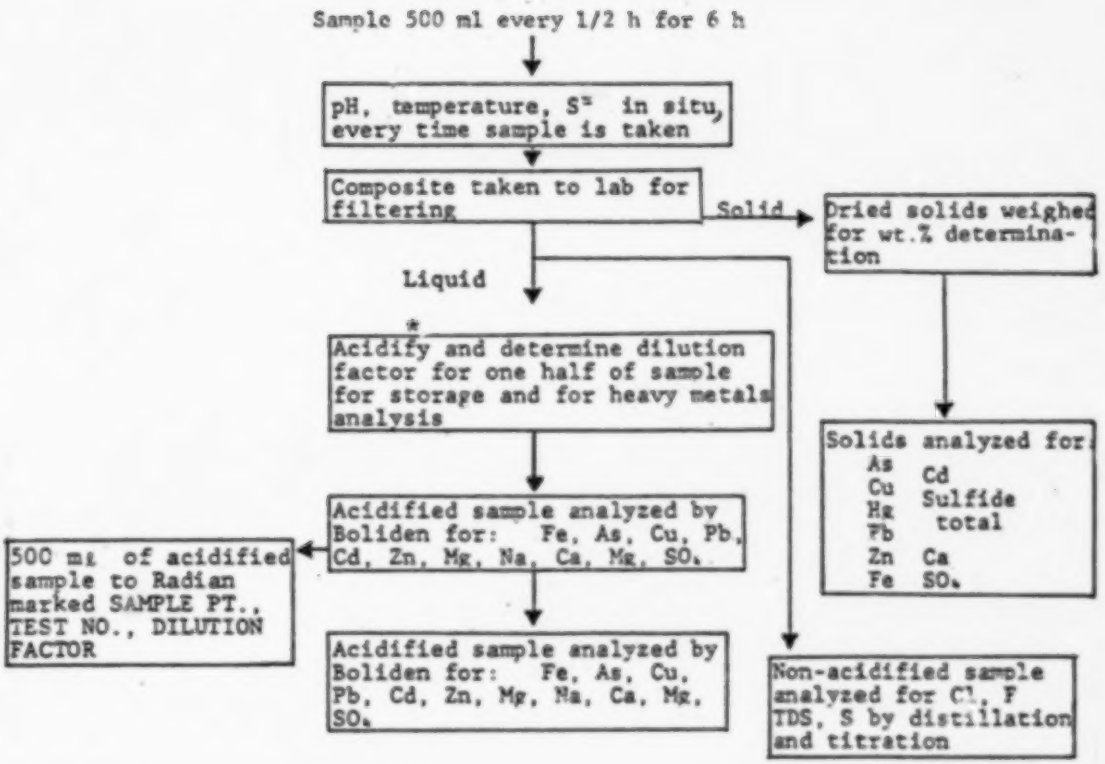

Sample 500 ml every 1/2 h for 6 h
pH, temperature, S= in situ, every time sample is taken
Composite taken to lab for filtering
Solid
Dried solids weighed for wt.% determination
Liquid
*
Acidify and determine dilution factor for one half of sample for storage and for heavy metals analysis
Solids analyzed for:
As Cd
Cu Sulfide
Hg total
Pb
Zn Ca
Fe SO4
Acidified sample analyzed by Boliden for: Fe, As, Cu, Pb, Cd, Zn, Mg, Na, Ca, Mg, SO4
500 ml of acidified sample to Radian marked SAMPLE PT., TEST NO., DILUTION FACTOR
Acidified sample analyzed by Boliden for: Fe, As, Cu, Pb, Cd, Zn, Mg, Na, Ca, Mg, SO4
Non-acidified sample analyzed for Cl, F TDS, S by distillation and titration

Figure 2. Sampling procedure for sample points 1 and 2 (process water and runoff water)

*Acidify with 25 ml 10 N HNO_3 per 2,500 ml sample.

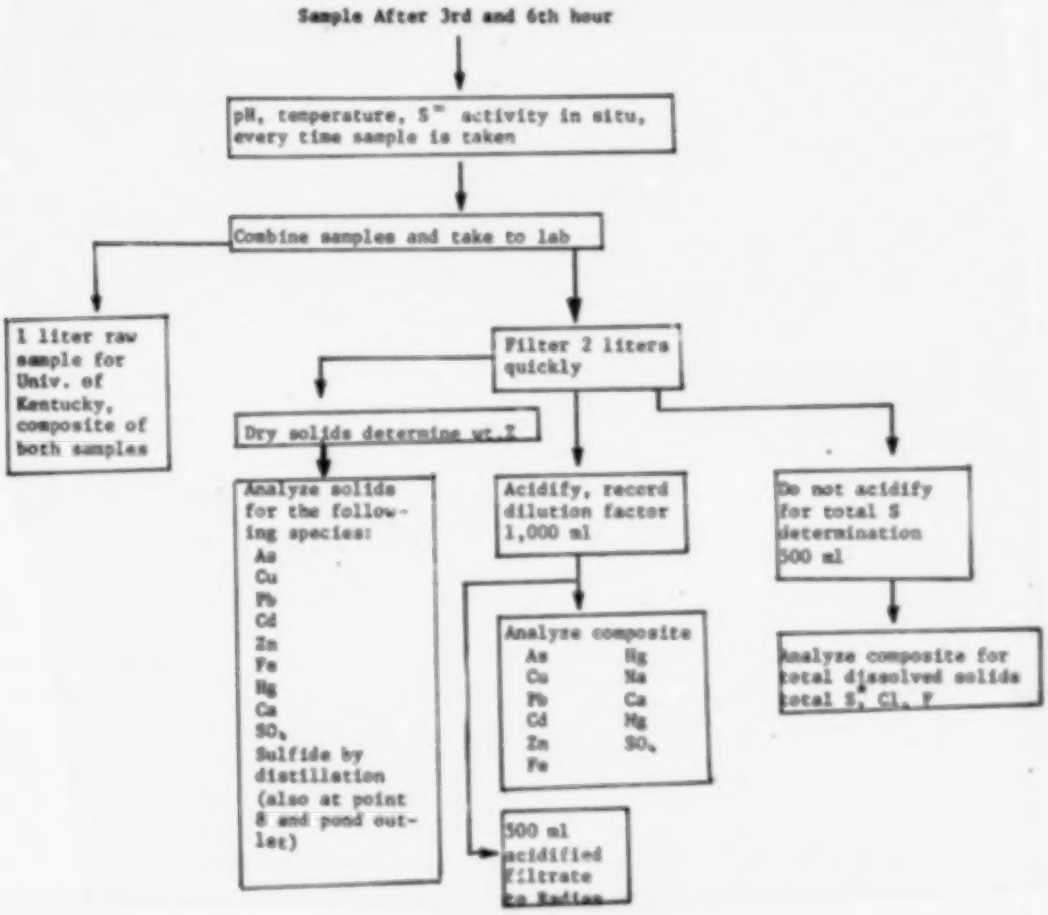

Sample After 3rd and 6th hour
pH, temperature, S= activity in situ, every time sample is taken
Combine samples and take to lab
1 liter raw sample for Univ. of Kentucky, composite of both samples
Filter 2 liters quickly
Dry solids determine wt.%
Analyze solids for the following species:
As
Cu
Pb
Cd
Zn
Fe
Hg
Ca
SO4
Sulfide by distillation (also at point 8 and pond outlet)
Acidify, record dilution factor 1,000 ml
Analyze composite
As Hg
Cu Na
Pb Ca
Cd Mg
Zn SO4
Fe
500 ml acidified filtrate to Radian
Do not acidify for total S determination 500 ml
Analyze composite for total dissolved solids total S, Cl, F

Figure 3. Sampling procedure for sample points 6, 7 and 8 (thickener overflow, filtered effluent, fluoride treatment effluent) and pond effluent[x].

*Total sulfide by distillation and titration. If concentrations are very low, use colorimetric method at Points 7 and 8.
[x]Pond effluent samples only once at the end of the test.

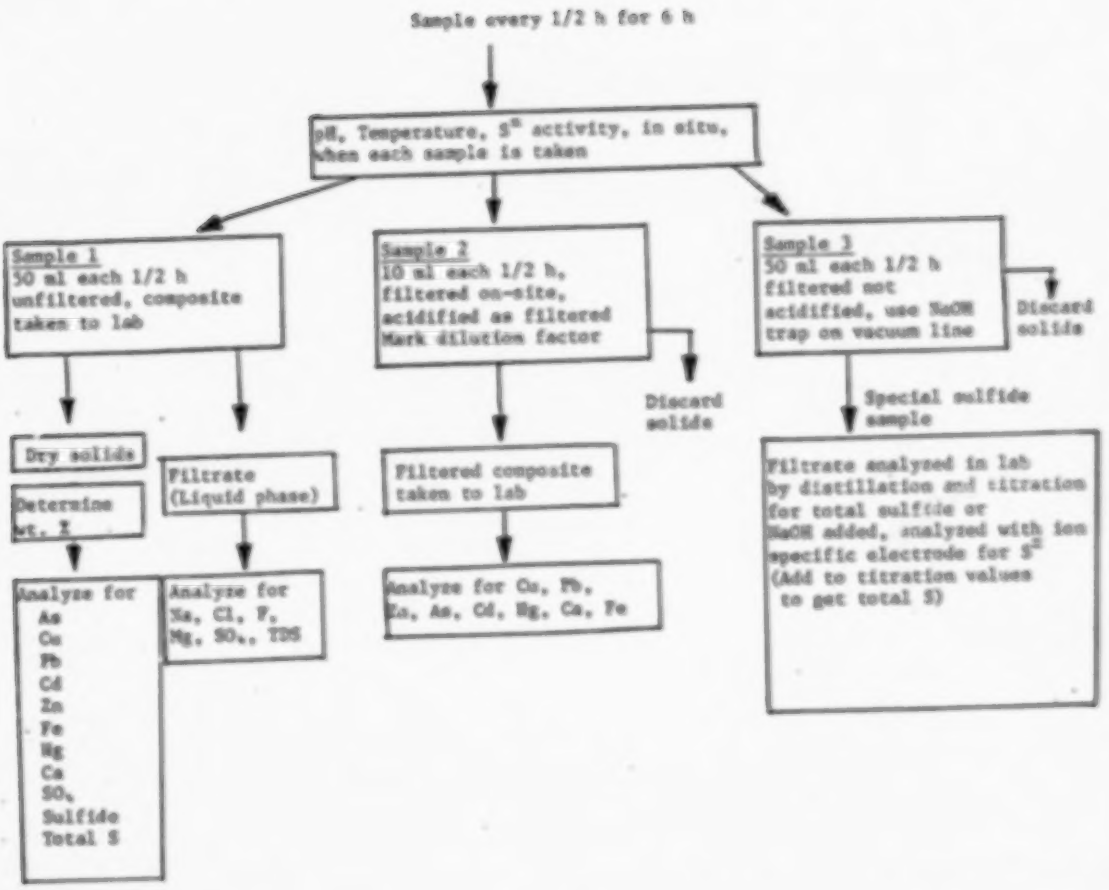

Sample every 1/2 h for 6 h
pH, Temperature, $S^{=}$ activity, in situ, when each sample is taken
Sample 1
50 ml each 1/2 h unfiltered, composite taken to lab
Sample 2
10 ml each 1/2 h, filtered on-site, acidified as filtered Mark dilution factor
Discard solids
Sample 3
50 ml each 1/2 h filtered not acidified, use NaOH trap on vacuum line
Discard solids
Special sulfide sample
Dry solids
Determine wt. %
Filtrate (Liquid phase)
Filtered composite taken to lab
Filtrate analyzed in lab by distillation and titration for total sulfide or NaOH added, analyzed with ion specific electrode for $S^{=}$ (Add to titration values to get total S)
Analyze for
As
Cu
Pb
Cd
Zn
Fe
Hg
Ca
SO_4
Sulfide
Total S
Analyze for Na, Cl, F, Mg, SO_4, TDS
Analyze for Cu, Pb, Zn, As, Cd, Hg, Ca, Fe

Figure 4. Sampling procedures for sample points 3, 4, and 5.

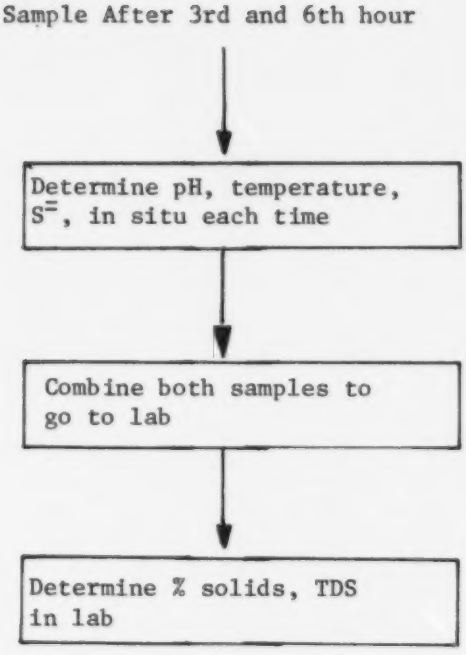
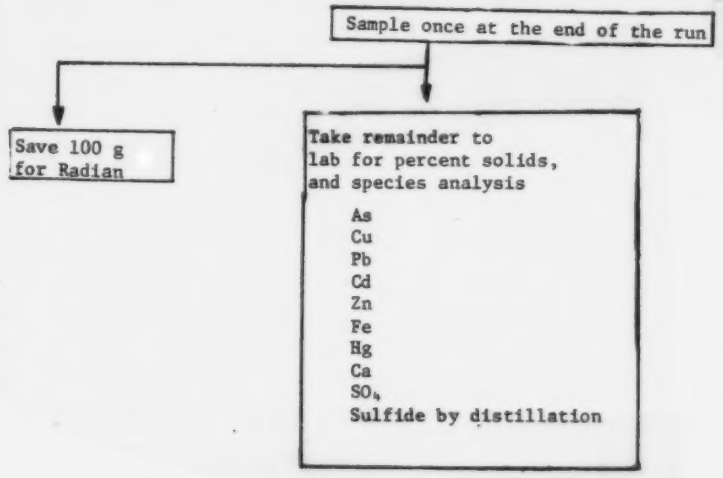

Sample After 3rd and 6th hour
Determine pH, temperature, $S^{=}$, in situ each time
Combine both samples to go to lab
Determine % solids, TDS in lab

Figure 5. Sampling procedure for sample point 9 (thickener underflow).

Sample Point 10



Special Short Test

SST 01: One grab sample at sampling points 1, 2, 5, 7, and 8

SST 02: Composite of six samples taken over 3-hour period

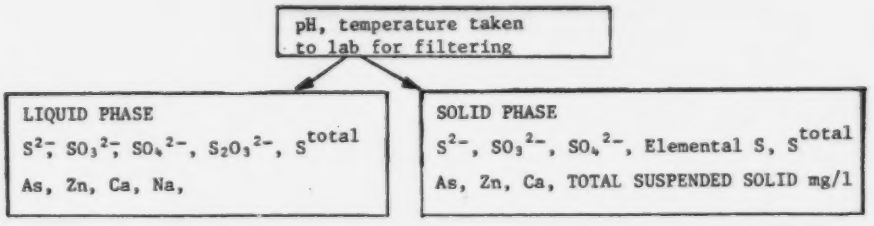

pH, temperature taken to lab for filtering
LIQUID PHASE
S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, S^{total}
As, Zn, Ca, Na,
SOLID PHASE
S^{2-}, SO_3^{2-}, SO_4^{2-}, Elemental S, S^{total}
As, Zn, Ca, TOTAL SUSPENDED SOLID mg/l

Figure 6. Sampling procedure for sample point 10 (filtered sludge out of drum filter) and for special short tests.

Mercury

Mercury in solution was reduced with stannous chloride ($SnCl_2$). Elemental mercury was stripped into a cell equipped with a mercury detector. The method is described by Hach and Ott(1).

Chloride and Fluoride

Ion sensitive electrodes were applied for quantitative determination of chloride and fluoride, using the method of standard addition.

Sulfide

The methylene blue method was chosen for sulfide determination. This colorimetric procedure is based on the reaction which takes place under suitable conditions between paraamino-dimethylaniline, ferric chloride and the sulfide ion. The intensity of the methylene blue formed is compared with standard methylene blue solutions.

The method is sensitive down to 50µg/ℓ sulfide. A detailed description is given in The Standard Methods for the Examination of Water and Waste Water (2).

Sulfide in solid samples was determined through a distillation and titration procedure. The sulfide is liberated through acidification and is then distilled into work bottles containing cadmium acetate. The cadmium sulfide precipitate formed is isolated by filtration. The sulfide is redissolved and determined iodometrically.

Sulfate

Sulfate was precipitated as $BaSO_4$ and determined gravimetrically.

Sulfite Plus Thiosulfate

The sum of sulfite plus thiosulfate was determined through an iodometric titration.

Thiosulfate

Sulfite is complexed by adding formaldehyde to the solution. The complex which is formed does not react with iodine. Thiosulfate is then determined iodometrically. The sulfite content is determined by difference.

Arsenic (III) also reacts with iodine. The results reported are corrected for this interference.

SECTION 4

RESULTS

The results of the tests will be discussed in the following sections: (1) a qualitative discussion of each test, describing general plant operation, unusual circumstances, upsets, etc.; (2) a summary of the test data; (3) a presentation and discussion of heavy metal removal results; (4) reagent consumption; (5) a survey of material and element balance calculations made on the results of the two more detailed tests, LT-01 and LT-02; (6) a short discussion about the side reactions of H_2S-SO_2; and (7) analytical results for organic priority pollutants.

Description of Tests

The following section will provide a qualitative discussion of the tests in chronological order. This discussion will also provide a comprehensive description of the plant operations during the two-week test period.

As was discussed in previous sections, the characterization program included two different types of tests:

- Three "short" tests, ST-01 through ST-03, in which two inlet locations and three outlet locations were sampled. The purpose of these tests was only to provide heavy metal removal and reagent consumption data.

- Two "long" tests, LT-01 and LT-02, in which a total of eleven sample points throughout the wastewater process were sampled. In addition to providing heavy metal removal and reagent consumption data, these results were to be the basis for material balance calculations.

The evaluation of the data indicated an SO_2-H_2S interaction. This prompted further testing at a later date by Boliden personnel to determine the amount of reaction products formed (thiosulfate, sulfur, polythionates).

Sample points upstream of the thickener were sampled every half hour throughout the test period. Sample points downstream of the thickener were sampled only once at the end of the test period. The five test days were chosen solely as days when the plant was operating properly; no effort was made to vary operating conditions from test to test. A description of each of these tests follows.

Test ST-01

The first test was a "short" test. The process water and plant runoff water were sampled to determine inlet conditions, and the effluent from the multimedia filters was sampled to determine outlet conditions for the sulfide process. The outlet of the lime treatment process and the outlet of the final settling pond were also sampled to determine outlet conditions for these two process steps.

The wastewater plant began operations at 7:00 a.m. on the morning of the first test. Due to a mechanical problem in the wastewater plant for two days prior to this start-up, all smelter wastewater flow had bypassed the wastewater plant and was disposed of in an effluent pond, where lime was added.

Sampling of inlet points and data recording for this first test began at 9:30 a.m. on January 30, 1979, 2½ hours after the plant started up. The plant outlet samples were taken 5 hours later or 7½ hours after start-up. This 7½ hours approaches the liquid residence time in the wastewater plant.

If a first order response on start-up of the plant can be assumed, regardless of what liquid concentrations were in the thickener and other downstream vessels after several days of dormancy, the outlet conditions sampled should have made a 60 percent approach to steady state conditions. The 7½ hours is negligible compared to the residence time of the final settling pond of several days, so the liquid-phase concentrations at this sample point were meaningless.

The vacuum filter treating the thickener underflow was started up briefly during the test, but was immediately shut down due to poor filter cake quality. The thickener is grossly oversized as far as solids residence time is concerned, so the plant can operate for several days without removing solids. The normal practice is to operate the vacuum filter only when the thickener underflow will form a sufficiently thick filter cake. Otherwise the solids level in the thickener is allowed to increase, resulting in a higher surface pressure at the underflow. However, as discussed in Section 2, Boliden was in the process of evaluating a polyelectrolyte during this period that proved to result in poor sludge handling properties.

The arsenic level in the plant influent water was relatively high during this test, over 400 mg/ℓ. At inlet arsenic levels of 300 to 400 mg/ℓ or greater, the plant begins to have sulfide dosage control problems. Under normal conditions, sodium sulfide addition is controlled by monitoring pH. As sodium sulfide is added, heavy metal sulfides form almost immediately, and no unreacted sodium sulfide remains in solution. However, as the heavy metals are consumed, excess sodium sulfide appears in solution and the pH begins to rise. By controlling sodium sulfide addition by pH, it can be added just to the point where the solution pH begins to rise significantly.

When arsenic is in the wastewater, its reaction with sodium sulfide is as follows:

$$3\ Na_2S + 2H_3AsO_3 \longrightarrow 6NaOH + As_2S_3\ .$$

The NaOH produced will cause a pH rise even while the sulfide is being consumed. When arsenic is present in high levels (over 200 mg/ℓ), a significant pH rise occurs before any excess sulfide is present. Since pH is used as a control parameter, the sulfide dosage added can be below the total stoichiometric requirement.

The inlet arsenic concentrations for Test ST-01 averaged 442 mg/ℓ. As will be discussed later in the section on reagent consumption, Test ST-01 is the only test of the five where the sulfide addition rate appears to be below the stoichiometric requirement. The stoichiometric sulfide requirement is the amount of sulfide which is theoretically required to react with all of the liquid-phase heavy metal content to form heavy metal sulfides. The results of this test also showed the highest outlet arsenic levels; this will be discussed in the section on removal data.

Test ST-02

This test was begun at 8:00 a.m. on January 31, over 24 hours after the plant was back in service. During the first hour of this test, an upset in a nearby lime system caused several temporary excursions of the pH in the plant runoff water hold tank from its normal 2 to 3 up to 7 to 8. These temporary excursions should not have significantly affected the results of the test.

The vacuum filter was started momentarily during the test but was again immediately shut down due to insufficient filter cake thickness. For the first two hours of the test, one of the two multimedia filters was stuck in the automatic backwash mode. Backwashing is accomplished with the filtered water from the sulfide process, before it goes to the lime treatment process. Since one filter was backwashing constantly for 2 hours, the flow to the lime treatment process was rather low. Much of the water treated by the sulfide process during these 2 hours was recycled back to the sulfide process inlet as backwash water, rather than flowing on to the lime treatment process.

Arsenic levels were normal during this test. The average inlet arsenic concentration to the plant was well below 200 mg/ℓ.

Test LT-01

This test was carried out on Friday, February 2. No testing was done on February 1 in order to let the smelter water lab catch up on a backlog of analyses. At the beginning of this test, the plant had been in continuous operation for over 3 days, so the final settling pond should have been approaching steady state heavy metal concentrations.

Arsenic levels during this test were below 200 mg/ℓ, so no sulfide addition control problems resulted. The vacuum filter again was not operated.

Test ST-03

The plant lime system was down from Saturday, February 3 to Tuesday, February 6. This test began one-half hour after the lime system was back in service. By the time the outlet of the lime treatment process was sampled, approximately 5 hours later, the tank had been at operating pH for over 2 hours. This was between two and three residence times through this vessel, so the sample should have been at near steady state conditions. The final settling pond was at an abnormally low pH (6.6) when sampled because of the preceding lime system outage. Again, liquid-phase results for this sample point were probably meaningless.

Test LT-02

The final test was performed the following day, Wednesday, February 7. In the first hour of the test, it was reported that an arsenic plant in the smelter was washing precipitators, so a high arsenic level was expected in the smelter runoff water stream entering the wastewater plant. The sulfide addition to the first reaction tank was increased in order to counteract the expected sulfide addition control problem previously discussed. However, the anticipated slug of arsenic never appeared in the plant inlet water, so the sulfide addition rate was greatly in excess of the amount required. Perhaps related to this large sulfide excess, the thickener overflow stream became rather cloudy; as a result, the sulfide addition rate was decreased and flow to the thickener and all downstream equipment was temporarily stopped. Flow was restored to the thickener and other downstream vessels (multimedia filters, lime treatment process, final settling pond) approximately one hour before these vessels were sampled at the end of the run.

Summary of Test Data

The operating data are summarized in Table 3. These data include the average wastewater flowrate through the sulfide process, the average flowrate through the lime treatment process, and the average pH of the incoming water streams, the reaction tanks, the thickener, and the lime treatment vessel for each test.

TABLE 3. OPERATING DATA SUMMARY OF HEAVY METAL REMOVAL TESTS‡

	TEST 1 ST-01 1/30/79	TEST 2 ST-02 1/31/79	TEST 3 LT-01 2/02/79	TEST 4 ST-03 2/06/79	TEST 5 LT-02 2/07/79
Total Inlet Rate (m^3/hr)*	114	128	108	143	131
Process Water Flow Rate (m^3/hr)†	40	60	31	43	39
Runoff Water Flow Rate (m^3/hr)†	74	68	77	100	92
Runoff Water pH	2.4	2.7	2.3	2.3	2.9
Reaction Tank I pH	3.7	3.7	3.9	4.9	4.2
Reaction Tank II pH	3.4	4.2	4.3	4.8	4.3
Reaction Tank III pH	3.7	4.1	4.0	3.9	4.1
Thickener Overflow pH	4.0	4.0	4.0	3.8	3.8
Lime Treatment pH	11.3	11.3	11.2	11.5	11.4
Settling Pond Effluent pH**	9.6	11.55	11.65	6.6	12.05

‡ The numbers presented are the arithmetic averages of the data taken on control room instruments over the duration of the sampling period.

*Design flow rate 200 m^3/hr maximum.

†Calculated by material balance on soluble species.

**pH of grab sample taken at the end of test.

Table 4 presents average residence times in each process vessel for each of the five tests. These residence times were calculated by dividing the volume of each vessel in m^3 by the average flow rate through that portion of the plant in m^3/h. For comparison, the duration of each test in hours is also included.

The analytical results are shown in Tables 5 through 9. The values are given in mg/ℓ unless otherwise noted.

Liquid samples of rain and wash water, process waters, the thickener overflow, multilayer filter effluent, fluoride precipitation tank effluent, and pond overflow were preserved by acidification, shipped to Radian and analyzed by plasma emission spectroscopy. This analytical method gives semiquantitative survey analyses for 32 elements. The results are presented in Table 10. The values agree well with the data obtained by Boliden's quantitative measurements. In addition, the values verify that the major heavy metals were covered in the tests. The sulfite values found at the exit of the fluoride plant were 316, 464, 416, and 320 mg/ℓ. The corresponding calcium concentrations were 234, 312, 188, and 247 mg/ℓ. The pH of the solution is 11.4 at this point. These data are very high in respect of the calcium sulfite ($CaSO_3 \cdot 1/2\ H_2O$) solubility of 45 mg/ℓ in water. Increasing the pH should decrease this value. Moreover, the solutions had practically no H_2S smell in spite of an addition in excess of the stoichiometric amounts. The results of the sulfide analyses are at the lower limit of the analytical method (0.1 mg/ℓ). Furthermore, the sulfur balances did not close. These facts prompted the performance of special tests SST-01 and SST-02, which had the goal of clarifying the fate of the sulfur species. Analyses were performed not only for sulfate, sulfite, and sulfide, but also for thiosulfate, and elemental and total sulfur. Thiosulfate is an intermediate, and elemental sulfur is the end product of the liquid-phase Claus reaction. The results are shown in Table 11.

Removal Data

The aqueous phase removal data for the five tests are presented in Tables 12 through 16. Heavy metal concentrations at the inlet to the plant, the outlet of the sulfide treatment section, and the outlet of the lime treatment (fluoride removal) section are included. Also, percent removal of each heavy metal based on aqueous phase concentrations is calculated across the sulfide section, across the lime treatment section, and across the two processes together.

Generally, the sulfide process was able to achieve high levels of removal of copper, lead, cadmium, and mercury. Removal of these metals by the sulfide process was down to, or at least very near, the detection limits of the analytical procedures. Arsenic removal by the sulfide process varied from 67 percent in Test ST-01 to 87 percent in Test ST-02. As discussed in the previous section, the lower arsenic removal in Test ST-01 was probably caused by the high inlet arsenic concentration and the resulting sulfide addition control problem. Zinc and iron removal by the sulfide

TABLE 4. AVERAGE RESIDENCE TIMES IN PROCESS VESSELS

Vessel/Test	Residence Time (Hours)				
	ST-01	ST-02	ST-03	LT-01	LT-02
Reaction Tank 1	0.5	0.4	0.4	0.5	0.4
Reaction Tank 2	0.4	0.3	0.3	0.3	0.3
Reaction Tank 3	0.5	0.4	0.3	0.5	0.4
Thickener	6.0	4.8	6.3	5.7	4.7
Thickener Overflow Tank	0.5	0.4	0.4	0.5	0.4
Multimedia Filters	0.4	0.3	0.3	0.4	0.3
Filter Backwash Tank	0.5	0.4	0.3	0.5	0.4
Total Sulfide Process	8.8	7.0	6.3	8.4	6.9
Lime Treatment Process	1.5	1.5	1.2	1.6	1.7
Total Wastewater Plant	10.3	8.5	7.5	10.0	8.6
Test Duration*	5.5	6	4.5	5.5	5.5

*Ideally, the test duration in each case should have been at least one residence time through the system. Test lengths were limited by the constraint that all sampling and sample preservation or immediate analyses be completed during the normal day shift.

TABLE 5. ANALYTICAL RESULTS FOR TEST ST-01

SHORT TEST No. ST-01 DATE 79-01-30

SAMPLE POINT NUMBER		1	2	7	8	FORD EFFLUENT	79-01-31 Na_2S	79-01-31 NaOH 50 %
LIQUID PHASE								
SAMPLE ID - A		ST-01-01-A	ST-01-02-A	ST-01-07-A	ST-01-08-A	ST-01- FORD EFFLUENT		
As	mg/l	600	148	146	19,1	130		
Cu	"	≤0,1	2,3	≤ 0,1	≤ 0,1	≤ 0,1		
Pb	"	10,5	1,0	≤ 0,2	≤ 0,2	≤ 0,2		
Cd	"	3,60	1,43	≤ 0,05	≤ 0,05	0,05		
Zn	"	38,5	32,0	39,0	≤ 0,5	0,5		
Fe	"	18,3	19,0	18,1	0,1	0,6		
Hg	"	0,019	3,4	0,011	0,011	0,006	≤0,05	
Na	"	760	1566	1305	1890	1225		NaOH
Ca	"	64,3	25,0	48,3	151	150		48,9 %
Mg	"	78,5	33,8	60,0	1,58	47,1		
SO_4	g/l	1,08	1,97	1,47	1,95	1,81		
SAMPLE ID - B								
Cl	g/l	1,96	0,96	1,16	1,18	1,14	NA	NA
F	mg/l	49,1	164,4	89,7	30,4	31,3	NA	NA
Sulfide	"	≤0,5	≤ 0,5	≤ 0,5 x	0,7 x	≤0,5		
Sulfite Jod+H_2SO_4	"	723,0	1760	NA	NA	NA	Na_2S 127g/l	NA
TDS	g/l	3,37	4,73	3,88	4,32	4,63	NA	NA
Solution pH							spc v_o 1,10³ 20°C	
SOLID PHASE								
SAMPLE ID - S		ST-01-01-S	ST-01-02-S	ST-01-07-S	ST-01-08-S			
As	Wt %	9,4	1,9	29,1	2,8 %	17,8	NA	NA
Cu	"	4,3	5,0	5,8	0,14 %	0,8	NA	NA
Pb	"	38,8	50,8	14,5	0,33 %	1,8	NA	NA
Cd	"	0,4	0,1	2,1	0,04 %	0,2	NA	NA
Zn	"	1,6	1,0	6,7	1,9 %	6,7	NA	NA
Fe	"	1,0	2,9	1,8	1,3 %	4,8	NA	NA
Hg	"	0,5	3,8	0,8	0,019 %	0,1	NA	NA
Na		NA	NA	NA	NA	NA	NA	NA
Ca	"	0,2	0,2	0,8	1,13 %	13,5	NA	NA
Mg		NA	NA	NA	NA	NA	NA	NA
SO_4		NS	NS	NS	13,9 %		NA	NA
Cl		NA	NA	NA	NA	NA	NA	NA
F		NA	NA	NA	2,82 %		NA	NA
Sulfide S		NS	NS	NS	10,3 %		NA	NA
Suspended solid	mg/l	66	52	11	1340	21	NA	NA

NS No sample available for analysis.
NA Not to be analyzed.
x Sulfide by distillation and colorimetric. on 7 and 8 only if necessary; otherwise, by distillation and titration.

TABLE 6. ANALYTICAL RESULTS FOR TEST ST-02

SHORT TEST No. ST-02 DATE 1979-01-31

SAMPLE POINT NUMBER		1	2	7	8	POND EFFLUENT	Na_2S	NaOH
LIQUID PHASE								
SAMPLE ID-A		ST-02-01	ST-02-02	ST-02-07	ST-02-08	ST-02-PE		
As	mg/l	133	107	16.0	1.8	36.3		
Cu	"	<0.1	0.9	<0.1	< 0.1	< 0.1		
Pb	"	7.4	1.2	<0.1	< 0.1	< 0.1		
Cd	"	9.5	1.55	< 0.01	< 0.01	< 0.01		
Zn	"	54.5	49.5	16.4	< 0.1	< 0.1		
Fe	"	5.7	11.2	7.9	0.2	< 0.1		
Hg	"	0.012	2.0	0.016	0.012	0.012		
Na	"	825	1013	1080	1068	1030		
Ca	"	116	34	49.3	234	206		
Mg	"	69.4	30.3	51.6	0.25	1.55		
SO_4	g/l	0.87	2.4	1.7	1.3	1.4		
SAMPLE ID-B		ST-02-1B	ST-02-2B	ST-02-7B	ST-02-8B	ST-02-Pond B		
Cl	g/l	1.40	0.83	1.13	1.16	1.14	NA	NA
F	mg/l	48.0	160	82.3	20.8	27.2	NA	NA
Sulfide	"	< 0.1	< 0.1	< 0.1 x	< 0.1 x	< 0.1		NA
Sulfite		288 mg/l	1370 mg/l	507 mg/l	316 mg/l	320 mg/l	NA	NA
TDS	g/l	3.30	3.66	3.85	3.68	3.86		
Solution pH								
SOLID PHASE								
SAMPLE ID - S		ST-02-01-S	ST-02-02-S	ST-02-07-S	ST-02-08-S	ST-02-Pond S		
As	wt%	7.7	4.9	<10	1.4%	5.2	NA	NA
Cu	"	2.1	8.1	<10	0.01%	1.0	NA	NA
Pb	"	54.7	44.0	<10	0.02%	1.9	NA	NA
Cd	"	0.9	0.1	< 0.1	0.003%	1.0	NA	NA
Zn	"	1.7	1.3	<10	2.10%	3.4	NA	NA
Fe	"	0.4	1.8	< 10	0.96%	4.2	NA	NA
Hg	"	0.3	2.6	2.4	0.003%	0.1	NA	NA
Na		NA	NA	NA	NA	NA	NA	NA
Ca		0.8	1.2	6	30.8%	5.7	NA	NA
Mg		0.05	0.1	2	5.4%	0.1	NA	NA
SO_4		NS	NS	NS	11.7%		NA	NA
Cl		NA	NA	NA	NA	NA	NA	NA
F		NA	NA	NA	4.8%		NA	NA
Sulfide	%	NS	NS	NS	8.0%		NA	NA
Suspended solid	mg/l	69	60	< 1	1870	14	NA	NA

NS No sample available for analysis.
NA Not to be analyzed.
x Sulfide by distillation and colorimetric. on 7 and 8 only if necessary; otherwise by distillation and titration.

TABLE 7. ANALYTICAL RESULTS FOR TEST ST-03

SHORT TEST No. ST-03 | DATE 1979-02-06 | START TIME | FINISH TIME

SAMPLE POINT NUMBER		1	2	7	8	POND EFFLUENT
LIQUID PHASE						
SAMPLE ID - A		ST-03-01	ST-03-02	ST-03-07	ST-03-08	ST-03-PE
As	mg/l	152	146	33.1	4.1	56
Cu	"	<0.1	1.2	<0.1	<0.1	<0.1
Pb	"	11.5	1.6	0.2	<0.1	0.4
Cd	"	4.95	3.1	<0.01	<0.01	0.02
Zn	"	32	36	15.0	<0.1	34
Fe	"	14.2	37.5	14.6	<0.01	3.6
Hg	"	0.13	4.1	0.044	0.01	0.012
Na	"	805	1017	1217	1450	1237
Ca	"	73.8	22.5	53.8	312	93.7
Mg	"	80.0	26.9	67.0	0.50	60
SO_4	g/l	1.22	2.96	1.97	2.13	1.68
SAMPLE ID - B						
Cl	g/l	1.30	0.97	1.23	1.20	1.20
F	mg/l	26.8	350	103	37.9	60.8
Sulfide	mg/l	<0.1	<0.1 x	<0.1 x	20.6 x	0.1
Sulfite	mg/l	350	1360	3360	4864	4864
TDS	g/l	3.51	6.12	4.47	4.96	4.32
Solution pH						
SOLID PHASE						
SAMPLE ID - S						
As	wt %	11.0	1.1	<1	4.7 %	7.0
Cu	"	4.0	2.2	<1	0.019 %	0.04
Pb	"	39.7	52.6	<4	0.025 %	0.2
Cd	"	0.3	0.2	<0.1	0.004 %	0.04
Zn	"	0.1	0.4	<1	3.0 %	3.5
Fe	"	1.6	0.9	<2	1.8 %	4.9
Hg	"	0.6	9.3	<1	0.0018 %	0.01
Na		NA	NA	NA	NA	NA
Ca		0.2	0.3	<5	24.3 %	28.0
Mg		NA	NA	NA	NA	NA
SO_4		NS	NS	NS	7.7 %	
Cl		NA	NA	NA	NA	NA
F		NA	NA	NA	NS	NS
Sulfide		NS	NS	NS	NS	NS
Suspended solid	mg/l	68	48	<1	185	36

NS No sample available for analysis.
NA Not to be analyzed.
x Sulfide by distillation and colorimetric. on 7 and 8 only if necessary; otherwise, by distillation and titration.
+ Sulfite values are too high due to thiosulfate interference.

TABLE 8. ANALYTICAL RESULTS FOR TEST LT-01

LOSO TEST No. LT-01 DATE 1979-03-02

SAMPLE POINT NUMBER		1	2	3	4	5	6	7	8	9	10	CaF_2 POND EFFLUENT
LIQUID PHASE												
SAMPLE ID-A		LT-01-01-A	LT-01-02-A	LT-01-03-A	LT-01-04-A	LT-01-05-A	LT-01-06-A	LT-01-07-A	LT-01-08-A			LT-01-PE
As	mg/l	181	143	31.4	28.3	29.4	29.3	37.8	1.9		NA	11.5
Cu	"	< 0.1	4.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		NA	< 0.1
Pb	"	8.2	0.3	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2		NA	< 0.2
Cd	"	4.5	1.35	0.02	0.02	< 0.02	0.02	0.03	0.02		NA	< 0.02
Zn	"	47.0	40.5	10.7	10.8	16.5	15.7	22.0	0.3		NA	0.3
Fe	"	6.5	11.5	5.7	5.7	6.0	7.5	7.2	< 0.1		NA	< 0.1
Hg	"	0.007	3.0	0.008	0.016	0.016	0.009	0.012	2.006		NA	0.010
Ca	"	63.8	4.3	47.5	43.8	45.0	46.3	41.3	188		NA	294
Na	"	613	2338	1163	1163	1175	1175	1225	1088		NA	1025
Mg	"	67.5	26.9	61.3	62.5	62.5	63.8	62.5	0.9		NA	1.3
SO_4	g/l	1.18	2.00	1.05	1.04	2.14	1.57	1.04	1.43		NA	1.36
SAMPLE ID-B												
Cl	g/l	1.24	0.92	1.12	1.10	1.14	1.09	1.12	1.13		NA	1.07
F	mg/l	54	272	231	233	225	224	220	26.0		NA	29.2
Sulfide	mg/l	< 0.1	< 0.1	0.1 x	< 0.1 x	< 0.1 x	< 0.1	< 0.1	< 0.1		NA	< 0.1
Sulfite	mg/l	200	1936	1424+	1794+	1634+	2164+	3154+	4164+		NA	2364+
TDS	g/l	3.19	4.95	4.28	4.41	4.49	3.98	4.87	4.26		NA	4.29
Solution pH												
SOLID PHASE												
SAMPLE ID-S		LT-01-01-S	LT-01-02-S	LT-01-03-S	LT-01-04-S	LT-01-05-S	LT-01-06-S	LT-01-07-S	LT-01-08-S	LT-01-09-S	LT-01-10-S	LT-01-PE
As	mg/g	9.1	3.9	37.3	34.8	35.9	31.6	< 1	1.26	NA	26.2%	0.78
Cu	"	4.2	6.2	1.3	1.1	1.9	2.3	< 1	< 0.01%	NA	1.9%	0.07
Pb	"	42.9	46.2	9.1	8.5	10.6	11.0	5	0.02%	NA	37.0%	0.14
Cd	"	4.0	0.03	1.1	1.0	1.3	1.2	< 0.1	0.0025	NA	1.2%	0.016
Zn	"	2.0	0.7	6.0	5.4	5.5	5.6	< 1	1.30%	NA	3.10%	0.42
Fe	"	0.5	1.4	0.6	0.6	0.5	0.7	2	0.63%	NA	0.63%	0.23
Hg	"	0.8	5.2	0.9	0.7	0.7	0.9	0.3	0.0008%	NA	0.60%	0.002
Na	"	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
Ca	"	0.1	1.0	0.4	0.4	0.0	0.3	6	0.03%	NA	2.1%	0.32
Mg	"	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
SO_4	"	NS	NS	NS	NS	NS	NS	NS	9.2%	NA	3.0%	
Cl	"	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
F	"	NA	NA	NA	NA	NA	NA	NA	5.0%	NA	NA	
Sulfide	%	NS	NS	NS	NS	NS	NS	NS	7.0%	NA	NA 14.0%	
Suspended solids	mg/l	44	36	260	230	245	35	< 1	1250	P_2O_5=90.0%	P_2O_5=16.5	6

NS No sample available for analysis.
NA Not to be analyzed.
x Sulfide by distillation and colorimetric on 7 and 8 only if necessary; otherwise by distillation and titration.
+ Sulfite values are too high due to thiosulfate interference.

TABLE 9. ANALYTICAL RESULTS FOR TEST LT-02

LONG TEST No. LT-02 DATE 1979-02-07

SAMPLE POINT NUMBER		1	2	3	4	5	6	7	8	9	10	CaF_2 POND effluent
LIQUID PHASE												
SAMPLE ID-A		LT-02-01-A	LT-02-02-A	LT-02-03-A	LT-02-04-A	LT-02-05-A	LT-02-06-A	LT-02-07-A	LT-02-08-A			
As	mg/l	143	102	27.0	22.4	18.8	20.3	24.2	1.9	NA	NA	9.4
Cu	"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	NA	NA	<0.1
Pb	"	9.2	4.8	0.6	0.5	0.1	<0.1	0.2	0.2	NA	NA	0.2
Cd	"	20.4	1.7	0.40	0.08	<0.01	<0.01	0.12	<0.01	NA	NA	<0.01
Zn	"	72	17.8	8.4	8.2	10.5	8.0	13.6	<0.1	NA	NA	<0.1
Fe	"	10.4	34	11.7	12.1	12.8	14.2	14.8	<0.1	NA	NA	<0.1
Hg	"	0.052	2.4	0.14	0.028	0.016	0.016	0.008	0.012	NA	NA	0.012
Ca	"	78	32.5	63	65.5	65.8	59.6	62.5	247	NA	NA	325
Na	"	755	1500	1175	1207	1237	1130	1163	1267	NA	NA	1212
Mg	"	73	73	66.3	67.1	70	65	65.9	2.1	NA	NA	2.00
SO_4	g/l	0.97	2.44	1.71	1.75	1.68	1.59	1.67	1.79	NA	NA	1.87
SAMPLE ID-B												
Cl	g/l	1.24	1.23	1.22	1.27	1.24	1.21	1.24	1.25	NA	NA	1.18
F	mg/l	16.8	330	98	98	97	89	86	26.2	NA	NA	22.2
Sulfide	mg/l	0.1	0.1	1.1 x	0.6 x	0.3 x	0.1	0.1	0.5	NA	NA	0.1
Sulfite	mg/l	261	1264	325+	326+	322+	270+	274+	320+	NA	NA	360+
TDS	g/l	3.40	5.04	4.31	4.49	4.15	3.96	4.08	4.40		NA	4.70
Solution pH												
SOLID PHASE												
SAMPLE ID-S		LT-02-01-S	LT-02-02-S	LT-02-03-S	LT-02-04-S	LT-02-05-S	LT-02-06-S	LT-02-07-S	LT-02-08-S	LT-02-09-S	LT-02-10-S	LT-02-Pond
As	Wt%	14.0	9.7	30.2	28.6	28.3	24.6	26.7	1.6%	NA	25.8%	5.3
Cu	"	5.8	5.6	1.2	1.1	1.9	1.6	3.4	0.005%	NA	2.2%	0.4
Pb	"	30.6	31.1	8.8	8.3	12.8	13.6	21.7	0.034%	NA	16.4%	0.8
Cd	"	0.8	0.4	4.0	4.4	2.9	2.9	3.4	0.005%	NA	2.0%	0.1
Zn	"	2.8	1.8	11.1	11.9	8.8	7.8	6.7	2.0%	NA	5.2%	1.1
Fe	"	1.2	1.2	0.6	0.6	0.6	0.7	1.0	1.1%	NA	0.73%	0.7
Hg	"	0.7	8.6	1.2	0.8	0.9	1.2	1.2	0.0023%	NA	0.98%	0.1
Na		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ca	"	0.06	0.9	0.2	0.2	1.0	1.0	1.9	15.3%	NA	2.2%	2.9
Mg		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SO_4		NS	NS	NS	NS	NS	NS	NS	5.7%	NA	<0.1%	
Cl		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
F		NA	NA	NA	NA	NA	NA	NA	5.3%	NA	NA	
Sulfide	S	NS	NS	NS	NS	NS	NS	NS	3.4%	NA	24.4%	
H_2O Wt%										95.9	80.0	
Suspended solid	mg/l	83	85	374	371	377	29	8	1350			

NS No sample available for analysis.
NA Not to be analyzed.
x Sulfide by distillation and colorimetric on 7 and 8 only if necessary; otherwise by distillation and titration.
+ Sulfite values are too high due to thiosulfate interference.

TABLE 10. ANALYTICAL RESULTS OF BOLIDEN SAMPLES BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY (ppm)

Description	Ag	Al	As	Au	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
ST1-01	<.005	.939	698	.035	.273	.016	170	3.64	<.15	.202	<.005	17.6	<10
ST1-02	<.005	.389	145	<.010	.152	.018	57.5	1.4	<.15	.321	2.38	17.5	<10
ST1-07	<.005	<.06	148	.017	.229	.016	118	.014	<.15	.298	<.005	17.1	<10
ST1-08	<.005	<.06	20.7	.015	.146	.045	393	<.005	<.15	<.005	<.005	.041	<10
ST1-P.E.	.014	.103	130	.086	.187	.020	470	<.005	<.15	.012	<.05	341	75.1
ST2-01	<.005	.349	126	.033	.134	.017	303	9.2	<.15	.119	<.003	5.34	<10
ST2-02	<.005	.359	107	<.01	.04	.016	75.5	1.54	<.15	.538	.895	11.2	<10
ST2-07	<.005	<.06	16.4	<.01	.031	.009	115	<.005	<.15	.283	<.005	8.01	<10
ST2-08	.010	<.06	.940	.072	.047	.043	538	<.005	<.15	<.005	<.005	.023	94.6
ST2-P.O.	<.005	<.060	31.2	.085	.172	.025	527	<.005	<.15	<.005	<.005	.025	84.7
ST3-01	<.005	1.48	147	.048	.273	.017	142	4.55	<.15	.462	.009	12.8	<10
ST3-02	<.005	<.06	139	<.01	.726	.008	40.6	2.73	<.15	6.17	.899	29.4	<10
ST3-07	.011	<.06	45.7	.040	.361	.008	98.1	<.005	<.15	1.8	<.005	13.5	<10
ST3-08	<.005	<.06	4.70	.044	.301	.016	516	<.005	<.15	<.005	<.005	.044	52.5
ST3-P.O.	<.005	<.06	95.6	<.01	.353	.006	183	<.005	<.15	.103	<.003	3.61	<10
LT1-01	<.005	.609	192	<.01	.223	.017	118	4.4	<.15	.127	<.005	7.38	<10
LT1-02	<.005	<.060	141	<.01	.203	.016	37.8	1.23	<.15	.465	3.98	12.3	<10
LT1-06	<.005	.223	48.49	<.01	.245	.004	81.8	<.005	<.15	.264	<.005	7.8	<10
LT1-07	<.005	<.06	44.3	<.01	.213	.005	73.4	<.005	<.15	.260	<.005	7.6	<10
LT1-08	.016	.066	1.41	.056	.219	.020	330	<.005	<.15	<.005	<.005	.042	76.1
LT1-P.	<.005	<.06	10.4	.054	.105	.018	466	<.005	<.15	<.003	.009	.012	73.9
LT2-01	<.005	1.00	143	<.01	.242	.016	150	19.0	<.15	.285	<.005	9.35	<10
LT2-02	<.005	.064	99	<.01	.683	.016	59.6	1.49	<.15	6.25	.068	30.2	<10
LT2-06	<.005	.619	22.1	.037	.293	.007	112	<.005	<.15	1.67	<.005	11.8	<10
LT2-07	<.005	.303	27.2	.023	.279	.006	120	.114	<.15	1.87	<.005	13.1	<10
LT2-08	<.005	<.06	.885	.019	.236	.016	457	<.005	<.15	<.005	<.005	.012	<10
LT2-P.O.	<.005	<.060	8.18	.029	.282	.014	540	<.005	<.15	<.005	<.005	.030	<10
LT1-10	3.83	300	6.3%	.63	4.1	.370	1.1%	2700.	13.5	37.6	4640	1460	5910
LT1-10*	13.4	1200	22%	17	18	.387	4.1%	9920	38.4	133	1.75%	4350	1.2%
LT2-10	6.55	1300	32%	16.3	23	.291	3.1%	1.6%	67.8	86.9	2.0%	3690	8770

*Filtered Sludge, Dry

(Continued)

TABLE 10. (Continued)

Decription	Mg	Mn	Mo	Na	Ni	Pb	Pt	Se	Si	Sn	Sr	Ti	U
ST1-01	148	.165	< .04	1400	.254	11.6	.11	.149	8.90	.978	.563	.023	< .30
ST1-02	67	.105	< .04	2400	.341	.700	.2	1.7	19.9	.72	.253	.014	< .30
ST1-07	118	.133	< .04	2140	.275	< .07	.11	.203	14.5	.582	.435	.025	< .30
ST1-08	.73	< .001	< .04	2900	< .02	< .07	< .1	< .12	7.8	.19	.41	.006	< .30
ST1-P.E.	87.1	.246	< .04	1811	.248	< .07	.12	< .12	11.0	.261	.444	.010	< .30
ST2-01	134	.134	< .04	1520	.117	6.0	.099	< .12	4.61	1.08	.596	.023	< .30
ST2-02	60.9	.101	< .04	1850	.538	.821	.81	1.48	12.9	.702	.252	.015	< .30
ST2-07	102	.111	< .04	1750	.232	< .07	.725	< .12	7.54	.377	.371	.018	< .30
ST2-08	.337	.004	< .04	1550	.08	< .07	.485	< .12	2.91	.195	.302	.013	< .30
ST2-P.O.	2.98	< .001	< .040	1680	.05	< .07	.052	< .120	3.18	.222	.459	.014	< .30
ST3-01	150	.211	< .04	1450	.425	.945	.23	.243	6.18	.541	.554	.027	< .30
ST3-02	56.2	.641	.459	3075	4.65	.886	.118	6.51	23.4	1.01	.210	.028	< .30
ST3-07	128	.298	< .04	2290	.860	< .07	.44	.277	9.59	.493	.410	.026	< .30
ST3-08	.416	.008	< .04	2320	.07	< .07	.22	< .12	5.08	.255	.45	.008	< .30
ST3-P.O.	117	.431	< .04	2050	.880	< .07	< .1	< .12	10.7	.45	.367	< .002	< .30
LT1-01	145	.098	< .04	1475	.157	6.32	.692	< .12	5.32	1.46	.526	.012	< .30
LT1-02	54.0	.082	< .04	2490	.478	< .07	.44	< .12	13.8	.811	.194	28.6	< .30
LT1-06	114	.084	< .040	2140	.222	< .07	.10	< .120	7.4	.510	.372	.016	< .30
LT1-07	117	.088	< .04	2100	.234	< .07	< .10	< .12	7.2	.620	.370	.014	< .30
LT1-08	.812	< .001	.084	2020	.046	< .07	.044	< .120	2.28	.172	.410	.012	.375
LT1-P.A	.932	< .001	< .040	1670	.050	< .07	.397	< .12	2.92	.185	.416	.008	< .30
LT2-01	144	.155	< .04	1570	.215	9.30	< .10	< .12	6.8	.37	.55	.017	< .30
LT2-02	85.3	.591	.274	2630	4.42	3.49	1.3	1.71	19.9	.643	.32	.022	< .30
LT2-06	131	.255	< .04	1840	.782	< .07	.47	.300	9.76	.262	.453	.024	< .30
LT2-07	132	.274	< .04	1980	.935	< .07	.47	.253	8.8	.282	.452	.023	< .30
LT2-08	4.01	.018	< .04	1990	.038	< .07	< .10	< .12	3.72	.169	.342	.004	< .30
LT2-P.O.	3.0	< .001	< .04	2010	.029	< .07	< .10	< .12	3.63	.227	.50	.006	< .30
LT1-10	825	5.3	64.3	3.2%	41.4	8750	11.4	994	34.	6482	18.1	5.7	1.6
LT1-10*	3220	16.8	234	12.2%	154	830	34.9	3890	10.	2960	1.85	14.0	2.02
LT2-10	3040	24.5	375	18.3%	348	1101	11.7	1150	396	1930	8.7	11.5	<1.5

* Filtered sludge, dry

(Continued)

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TABLE 10. (Continued)

Description	V	W	Zn	Zr	Sb	Bi	Hg	Totals
ST1-01	.164	.179	33.0	< .005	1.2	< .5		
ST1-02	.080	.092	28.5	< .005	1.9	< .5		
ST1-07	.135	.143	34.2	< .005	1.0	< .5		
ST1-08	.015	.041	.079	< .005	.8	< .5		
ST1-P.E.	.112	.096	.476	< .005	1.5	< .5		
ST2-01	.151	.054	48.7	< .005	1.3	< .5		
ST2-02	.062	.058	44.9	< .005	1.7	< .5		
ST2-07	.108	.043	15.2	< .005	1.4	< .5		
ST2-08	.019	.114	.013	< .005	0.7	< .5		
ST2-P.O.	.028	.162	< .002	.143	0.7	< .5		
ST3-01	.171	.138	28.5	< .005	1.0	< .5		
ST3-02	.074	.209	32.9	< .005	1.2	< .5		
ST3-07	.154	.155	14.2	< .005	.8	< .5		
ST3-08	.021	.060	.082	< .005	.7	< .5		
ST3-P.O.	.125	< .04	29.3	< .005	1.1	< .5		
LT1-01	6.59	< .04	45.0	< .005	2.0	< .5		
LT1-02	.047	.063	35.1	< .005	1.6	< .5		
LT1-06	.130	.061	13.9	.017	1.4	< .5		
LT1-07	.117	< .04	18.6	< .005	1.4	< .5		
LT1-08	.031	.123	.071	.017	0.8	< .5		
LT1-P.O.	.019	.125	.038	< .005	0.7	< .5		
LT2-01	.158	.067	63.3	< .005	1.1	< .5		
LT2-02	.099	.247	16.4	< .005	.7	< .5		
LT2-06	.158	.169	7.59	< .005	.5	< .5		
LT2-07	.150	.115	13.0	< .005	.7	< .5		
LT2-08	< .01	.044	< .005	< .005	< .5	< .5		
LT2-P.O.	< .01	< .04	.027	< .005	< .5	< .5		
LT1-10	3.05	28.6	7800	3.94	11	15		
LT1-10*	10.6	67.5	2.8%	1.7	29	42		
LT2-10	6.8	84.7	4.2%	.743	22	32		

* Filtered sludge, dry

TABLE 11. RESULTS OF SPECIAL SHORT TESTS SST-01 AND SST-02

	Rain and Washwater Point 01	Process Water Point 02	After Tank III Point 05	After Multi-layer Filter Point 07	Fluoride Treatment Effluent Point 08
TEST SST-01					
Liquid Phase, mg/ℓ					
Sulfate, as S	174	1890	379	325	282
Sulfite, as S	7	275	85	40	21
Sulfide, as S	NA	NA	—	—	—
Thiosulfate, as S	0	0	34	85	85
Total Sulfur, as S	180	2010	430	433	403
As	65	1330	17	14	3.8
Zn	33	463	71	49	0.07
Ca	52.4	44.5	50	50.6	223
Solid Phase					
Sulfate, wt% as S	2.5	6.9	0.3	—	1.8
Sulfide, wt% as S	19.4	2.5	21.3	—	3.0
Elemental Sulfur, wt% as S	NA	0.2	4.0	NA	0.4
Total Sulfur, wt% as S	—	10.0	35.2	12.5	4.2
Total Suspended Solid, mg/ℓ	42	908	1510	2	504
Waste Water Flow Rate m^3/h	70	40	NA	NA	NA
Na_2S Consumption, Kg/h as Na_2S	110	—	—	—	—
pH	2.45	1.99	3.7	4.2	10.0
TEST ST-02					
Liquid Phase, mg/ℓ					
Sulfate, as S	700	573	597	630	603
Sulfite, as S	165	505	410	385	175
Sulfide, as S	NA	NA	—	—	—
Thiosulfate, as S_2O_3	NA	NA	0	0	0
Total Sulfur, as S	955	1170	1080	1090	850
Ca	105	22.5	66.3	66.3	287
Solid Phase					
Sulfate, wt% as S	3.5	1.1	0.4	—	2.7
Sulfide, wt% as S	—	8.3	14.6	—	6.3
Total Sulfur, wt% as S	17.8	10.7	31.4	—	8.9
Total Suspended Solid, mg/ℓ	39	730	1800	4	1770
Waste Water Flow Rate m^3/h	75	35	NA	NA	NA
Na_2S Consumption, kg/h as Na_2S	78	—	—	—	—
pH	2.8	2.25	4.15	4.3	10.5

TABLE 12. TEST 1 (ST-01) HEAVY METAL REMOVAL DATA*

Element	Combined Inlet mg/ℓ	Outlet From Sulfide Process mg/ℓ	Outlet From Lime Treatment mg/ℓ	Percent Removal Sulfide Process	Percent Removal Lime Treatment	Overall Percent Removal
As	442	146	19.1	67	87	96
Cu	0.9	<0.1	<0.1	>90	-	>90
Pb	7.1	<0.2	<0.2	>97	-	>97
Cd	2.85	<0.05	<0.05	>98	-	>98
Zn	36.2	9.0	<0.5	-0-	>99	>99
Fe	18.5	18.1	0.1	2	99+	99+
Hg	1.2	0.01	0.011	99	-	99+
Mg		60.0	1.88		97	
F		89.7	34.4		62	
Ca		48.3	157			

* Total Metals

TABLE 13. TEST 2 (ST-02) HEAVY METAL REMOVAL DATA*

Element	Combined Inlet mg/ℓ	Outlet From Sulfide Process mg/ℓ	Outlet From Lime Treatment mg/ℓ	Percent Removal Sulfide Process	Percent Removal Lime Treatment	Overall Percent Removal
As	122	16.0	1.8	87	89	99
Cu	0.4	<0.1	<0.1	>75	-	>75
Pb	4.5	<0.1	<0.1	>98	-	>98
Cd	5.7	<0.01	<0.01	>99	-	>99+
Zn	52.2	16.4	<0.1	69	>99	>99+
Fe	8.3	7.9	0.2	5	97	98
Hg	0.9	0.016	0.012	98	25	99
Mg		51.6	0.25		99+	
F		82.3	20.8		75	
Ca		49.3	234			

* Total Metals

TABLE 14. TEST 3 (LT-01) HEAVY METAL REMOVAL DATA*

Element	Combined Inlet mg/ℓ	Outlet From Sulfide Process mg/ℓ	Outlet From Lime Treatment mg/ℓ	Percent Removal Sulfide Process	Percent Removal Lime Treatment	Overall Percent Removal
As	170	37.8	1.9	78	95	99
Cu	1.2	<0.1	<0.1	>92	-	>92
Pb	5.9	<0.2	<0.2	>97	-	>97
Cd	3.6	0.03	<0.02	99+	<33	>99+
Zn	45.1	22.0	0.3	51	98	99+
Fe	7.9	7.2	<0.1	9	>99	>99
Hg	0.9	0.012	0.008	99	33	99+
Mg		62.5	0.9		99	
F		120	26.0		78	
Ca		41.3	188			

* Total Metals

TABLE 15. TEST 4 (ST-03) HEAVY METAL REMOVAL DATA*

Element	Combined Inlet mg/ℓ	Outlet From Sulfide Process mg/ℓ	Outlet From Lime Treatment mg/ℓ	Percent Removal Sulfide Process	Percent Removal Lime Treatment	Overall Percent Removal
As	150	33.1	4.1	78	88	97
Cu	0.4	<0.1	<0.1	<75	-	>75
Pb	8.6	0.2	<0.1	98	>50	>99
Cd	4.4	<0.01	<0.01	>99+	-	>99+
Zn	33	15.0	<0.1	55	>99	>99+
Fe	19.7	14.6	<0.01	26	>99+	>99+
Hg	1.3	0.044	0.01	97	77	99+
Mg		67.0	0.5		99+	
F		103	32.9		68	
Ca		53.8	312			

* Total Metals

TABLE 16. TEST 5 (LT-02) HEAVY METAL REMOVAL DATA*

Element	Combined Inlet mg/ℓ	Outlet From Sulfide Process mg/ℓ	Outlet From Lime Treatment mg/ℓ	Percent Removal Sulfide Process	Percent Removal Lime Treatment	Overall Percent Removal
As	131	24.2	1.9	82	92	99
Cu	<0.1	<0.1	<0.1	-	-	-
Pb	78	0.2	0.2	99+	-	99+
Cd	14.8	0.12	<0.01	99+	>92	>99+
Zn	55	13.6	<0.1	75	>99+	>99+
Fe	17.5	14.8	<0.1	15	>99+	>99+
Hg	0.8	0.008	0.012	99	99+	99
Mg		65.9	2.1			
F		86	26.2			
Ca		62.5	247			

* Total Metals

process was generally low, with zinc removal ranging from 0 to 75 percent. These low levels of removal are apparently a result of the low pH at which the sulfide process was operated, generally 4.0 or less.

The only significant heavy metal content in the inlet to the lime treatment process was arsenic, zinc, and iron. Arsenic removal by the lime treatment process varied from 87 to 95 percent, resulting in combined arsenic removal levels of 96 percent and greater. Removal of zinc and iron by the lime treatment process varied from 97 percent to over 99 percent.

Also included in Tables 12 through 16 are the fluoride removal data across the lime treatment section for each of the five tests. The observed fluoride removal across the lime treatment section ranged from 62 to 78 percent.

These results are indicative of the combined effectiveness of the sulfide and lime processes in removing heavy metal content from the aqueous phase of smelter wastewater. However, the actual effluent from the Boliden smelter also included some solids containing heavy metals. Solid-liquid separation after the lime treatment process was achieved in a settling pond with a residence time of several days. The outlet from this pond was sampled at the end of each test, and the liquid and solid phases were analyzed. The liquid-phase pond concentrations for Test LT-01 represent the results of over three days of continuous operation, and therefore should represent an approach to steady-state concentrations. The pond outlet concentrations of all heavy metals except arsenic are at the same levels as the outlet concentrations for the lime treatment process for Test LT-01. The arsenic level at the pond outlet for this test was 11.5 mg/ℓ, while the arsenic level at the outlet of the lime treatment process was only 1.9 mg/ℓ. This higher arsenic level was probably due to the fact that the pond throughput at low arsenic levels had not been sufficient to purge earlier high concentrations.

The solid-phase heavy metal carry-over results from all five tests can be assumed to be typical. The heavy metal concentrations in the pond liquid-phase are relatively dilute, but the pond is a reservoir for several months worth of heavy metal solids. Large changes in the heavy metal content of the pond liquid-phase should have little overall effect on the pond solids. Consequently, solids carry-over should be related more to pond throughput and solids particle size and should have been profoundly affected by periods when the treatment plant was not in normal operation, as were the liquid-phase results. The range of solid-phase heavy metal carry-over results are reported in Table 17.

In summary, the wastewater plant at Boliden did not operate long enough for any period of time to permit the sampling of actual pond overflow liquid which fully corresponded to continuous plant operation. However, the results of Test LT-01 indicate that the heavy metal emissions from the overflow pond during continuous normal operation can be approximated by summing the liquid-phase heavy metal concentrations in Tables 12 through 16 and the solid-phase concentrations in Table 17.

TABLE 17. SETTLING POND OUTFLOW SOLIDS CONTENT, RANGE FOR FIVE TESTS

Component	Range for Five Tests (mg/liter of pond outflow liquor)
As	0.7-3.7
Cu	0.01-01
Pb	0.08-0.37
Cd	0.013-0.15
Zn	0.19-1.4
Fe	0.11-1.7
Hg	0.003-0.016
Ca	0.49-9.5
Total Solids	14-34
Apparent Percent Solids Removal Across Pond	81.6*-99.5 percent.

*This low value corresponded to one test where the solids content of the lime treatment process outlet appeared to be abnormally low. The apparent percent removals for the other four tests were in excess of 98 percent.

Reagent Consumption

Reagent consumption rates could generally not be measured accurately within the time frame of these tests. In fact, sodium hydroxide consumption could not be measured at all.

There are no flow meters on the sodium hydroxide feed lines, and the level indicator on the supply tank was not in operation during the test period. Also, due to the high sodium levels in the plant water, a sodium balance to determine consumption was not possible; that is, the change in concentration due to sodium hydroxide addition was on the order of the analytical accuracy. Sodium hydroxide consumption could be measured by totalling the caustic shipments to the plant over several months, but such measurements were not possible during our two-week test program.

Sodium sulfide consumption could be estimated for each daily test, but the accuracy of these estimates is questionable. Sulfide was added to the process from a day tank that had no level indicator. The tank was on level control, and was refilled automatically after the level had dropped 20 cm from full. This day tank was refilled from a mix tank which did have a level indicator. The sulfide consumption could then be calculated from the total of the sulfide in the drums added to the mix tank during the run and the sulfide contained in any change (negative or positive) in the level of the mix tank. However, some error was introduced in that the level of the day tank at the beginning and end of the test was not known. This level could have changed by as much as 20 cm during the course of a test.

Sulfide consumption data are present in Table 18 as milligrams of sodium sulfide added per liter of wastewater and as a stoichiometry: milliequivalents of sulfide added per milliequivalent of heavy metals in the wastewater. Also in Table 18 are the error limits of the stoichiometry numbers. The upper stoichiometry limit would result if the day tank level was at its highest point at the beginning of the test and at its lowest point (20 cm lower) at the end of the test. The lower stoichiometry limit would result if the tank had been at its lowest level at the beginning and its highest level at the end of the test. These values show the inaccuracy of the sulfide consumption numbers.

With the exception of Test ST-01, all of the stoichiometries are near or greater than one, indicating that an excess of sulfide had been added. In some tests, the sulfide dosage seems to have been two or three times what was required. In spite of this, the smell of the H_2S in the samples was either very faint or non-existent, indicating the consumption of sulfide by side reactions and/or the loss of H_2S to the plant ventilation system. Also, the non-closure of the sulfide balance, discussed later in the section on sulfite-sulfide interaction, is further evidence of such side reactions or losses; all of the sulfide added to the reaction tanks cannot be accounted for. Apparently side reactions account for most of these sulfide losses, as Boliden has since measured sulfide losses to the ventilation system to be less than 30 g/h, an insignificant amount.

TABLE 18. SULFIDE CONSUMPTION

Test Number	ST-01	ST-02	ST-03	LT-01	LT-02*
Sodium sulfide addition rate, mg/ℓ of wastewater	610	520	400	780	940
Calculated sulfide stoichiometry, milli-eq/milli-eq heavy metal	0.8	1.9	1.3	2.4	2.8
Lower limit sulfide stoichiometry	0.5	1.4	0.8	1.8	2.4
Upper limit sulfide stoichiometry	1.1	2.4	1.8	2.9	3.3

* Sulfide addition rate during LT-02 was manually raised to compensate for an expected rise in inlet arsenic that never occurred.

Note in Table 18 that the sulfide dosage in Test ST-01 appears to have been considerably lower than the other tests. As mentioned in Description of Tests, Test ST-01 was the only test where a high arsenic level in the inlet wastewater was encountered. The low sulfide dosage is evidence of the sulfide control problem which results when the plant arsenic levels approach or exceed 400 mg/ℓ.

Lime consumption data were calculated by calcium balance across the fluoride removal section. The lime silo and slakers were not equipped with flow measurement equipment and the lime silo was large enough that it was not often filled. Consequently, there was no way to measure lime addition rates physically. The lime addition rates based on calcium analyses before and after the lime treatment sections are presented in Table 19.

TABLE 19. LIME REAGENT DOSAGE

Test Number	ST-01	ST-02	ST-03	LT-01	LT-02
Lime Dosage, g CaO/m^3 Wastewater	174*	721	706	221*	549
Lime Treatment Outlet pH	11.45	11.55	12.0	11.60	11.40

* A charge balance on the solids in the outlet of the lime treatment process for these two tests shows an insufficient quantity of cations. This could be an indication that the solid-phase calcium percentages reported are low.

As will be discussed in Section 4.5, solid phase material balance calculations indicate that calcium analyses at the outlet of the fluoride removal or lime treatment section could be in error for Tests ST-01 and LT-01. The actual lime dosages for these tests may be much higher than the values in Table 19. Also, it should be noted that the liquid-phase calcium concentrations reported by Boliden are much lower than those determined later by Radian by inductively coupled plasma emission spectroscopy. These discrepancies place serious doubts as to the accuracy of the lime dosage estimates reported in Table 19.

Material balance calculations indicate that solid-phase calcium analyses on the lime treatment outlet for Tests ST-02 and ST-03 are reasonably accurate. Consequently, the results of these two tests have been used to estimate the excess lime, CaO, in the solids leaving the lime treatment section. For Test ST-02, the excess lime was estimated at 200 mg/ℓ as CaO. For Test ST-03, this estimate is 50 mg/ℓ as CaO. From these results, it appears that anywhere from 5 to 30 percent of the lime added in the fluoride removal or lime treatment section passes through and leaves the system as unreacted $Ca(OH)_2$ solids or as unslaked CaO.

The findings of the January/February test were checked by plant personnel in May and June, 1979. The sodium sulfide consumption in May was compared with the average metal precipitation. The following results were found in May:

Average arsenic concentration	200 mg/ℓ
Average zinc concentration	162 mg/ℓ
Other elements	40 mg/ℓ.

This element load consumes 580 mg/ℓ Na_2S or 0.97 kg of 60 percent Na_2S/solution per cubic meter of wastewater. The total wastewater treated in May was 62,280 m^3. The consumption of Na_2S totaled 427 barrels. This translated to the following consumption figures:

- Real consumption 68.3 metric tons as 60% Na_2S
- **Theoretical demand 61.1 metric tons as 60% Na_2S.**

The figures for June are as follows:

Average arsenic concentration	175 mg/ℓ
Average zinc concentration	20 mg/ℓ
Other elements	30 mg/ℓ
Sodium sulfide consumption	330 mg Na_2S/ℓ
	= 0.55 kg/m^3 (60% Na_2S)

Total flow	83020 m^3
Number of sodium sulfate barrels	354
Theoretical demand	45.7 tons as 60% Na_2S
Actual consumption	56.6 tons as 60% Na_2S.

The consumption of lime was not possible to average in this way due to problems with the lime slakers. The consumption of sodium hydroxide was 66 tons of 50 percent solution in May (0.53g NaOH per liter of wastewater) and 83 tons of 50 percent solution in June (0.50g NaOH per liter of wastewater).

Material Balance Data

Tests LT-01 and LT-02 were designed to be more detailed studies of the sulfide process, in which all major streams were to be sampled. These data were to be used with wastewater flow-rate and reagent addition rate data to calculate overall material and element balances. These balances were severely compromised by several factors:

1) The residence time of solids in the thickener was several days.

2) The Na_2S addition rate could only be measured roughly.

3) The lime addition rate had to be deduced by material balance.

4) The NaOH addition rate was not measurable.

5) Sulfide reacts with sulfite to form thiosulfate, polythionates and/or sulfur. No analyses were made to quantify these reaction products.

In spite of these problems, the following calculations could be made:

1) The balances across each reaction tank were calculated for Tests LT-01 and LT-02.

2) The stoichiometry between heavy metals and sulfide in the vacuum filter solids was checked.

3) The element balances around the lime treatment process were calculated.

4) The lime addition rate was calculated based on calcium analyses.

5) A sulfide material balance was attempted.

Reaction Tank Element Balances

During Tests LT-01 and LT-02, the outlets of all three reaction tanks were sampled, and both the liquid and solid phases analyzed. Unfortunately, the sample volume chosen to filter for solids analyses proved to be insufficient for solid sulfide determinations. The outlet of Tank 3 was sampled again at a later date, and the volume filtered was chosen such that the amount of solids collected was sufficient for a sulfide determination test. The sulfide in this sample was 80 percent of the stoichiometric ratio indicated by the heavy metals present in the precipitate.

Element balances were calculated across each of the three reaction tanks for both of the detailed tests. Agreement was generally good. Table 20 shows an element balance around Tank 1. Tables 21 and 22 present the results for the element removal from the liquid phase in the reaction tanks and the thickener.

TABLE 20. ELEMENT BALANCE DATA ACROSS REACTION TANK 1, TEST LT-01

Element	Combined Inlet to Reaction Tank 1			Outlet of Reaction Tank 1			Percent Closure
	Liquid Phase mg/ℓ	Solid Phase mg/ℓ	Total mg/ℓ	Liquid Phase mg/ℓ	Solid Phase mg/ℓ	Total mg/ℓ	
As	170	3.0	173	31.4	136	167	97
Cu	1.2	2.5	3.7	0.1	4.7	4.8	130
Pb	5.9	21.4	27.3	0.2	33.2	33.4	122
Cd	3.6	1.2	4.8	0.02	3.9	3.9	81
Zn	45.1	0.7	45.8	10.7	21.8	32.5	71
Fe	7.9	0.4	8.3	5.7	1.4	7.1	86
Hg	0.9	1.2	2.1	0.07	3.2	3.3	157

Note in Tables 21 and 22 the copper, lead, and iron appear to precipitate to an equilibrium concentration in the first reaction tank. Arsenic, cadmium, and mercury seem to show additional precipitation in Tanks 2 and 3, indicating that the wastewater leaving Tank 1 is not in

TABLE 21. LIQUID PHASE HEAVY METAL AND SULFIDE ANALYSES ACROSS REACTION TANKS AND THICKENER, TEST LT-01

	Into Reaction Tank 1 mg/ℓ	Out of Reaction Tank 1 mg/ℓ	Out of Reaction Tank 2 mg/ℓ	Out of Reaction Tank 3 mg/ℓ	Overflow from Thickener mg/ℓ
As	170.	34.1	28.3	29.4	39.3
Cu	1.2	<0.1	<0.1	<0.1	<0.1
Pb	5.9	<0.2	0.2	<0.2	<0.2
Cd	3.6	0.02	0.02	<0.02	0.02
Zn	45.1	10.7	10.8	16.5	15.7
Fe	7.9	5.7	5.7	6.0	7.5
Hg	0.9	0.068	0.016	0.016	0.020
S	--	0.1	<0.1	<0.1	<0.1

TABLE 22. LIQUID PHASE HEAVY METAL AND SULFIDE ANALYSES ACROSS REACTION TANKS, TEST LT-02

	Into Reaction Tank 1 mg/ℓ	Out of Reaction Tank 1 mg/ℓ	Out of Reaction Tank 2 mg/ℓ	Out of Reaction Tank 3 mg/ℓ	Overflow from Thickener mg/ℓ
As	131.	27.0	22.4	18.8	20.3
Cu	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	78.	0.6	0.5	0.1	<0.1
Cd	14.8	0.4	0.08	<0.01	<0.01
Zn	55.	8.4	8.2	10.5	8.0
Fe	17.5	11.7	12.1	12.8	14.2
Hg	0.8	0.14	0.028	0.016	0.016
S	--	1.1	0.6	0.3	0.1

solid-liquid equilibrium with respect to these elements. In both tests, the liquid-phase concentration of zinc actually appeared to increase across Tank 3.

Solids Analyses

The thickener underflow and vacuum filter solids were analyzed to determine weight percent solids for both Tests LT-01 and LT-02. This is a measure of the extent of dewatering in the thickener and vacuum filter. The results are summarized in Table 23.

TABLE 23. WEIGHT PERCENT SOLIDS IN THICKENER UNDERFLOW AND VACUUM FILTER SLUDGE

	Weight Percent Solids	
	Test LT-01	Test LT-02
Thickener Underflow	7.1	4.1
Vacuum Filter Sludge	23.5	20.0

The vacuum filter solids were also analyzed to determine the heavy metal and sulfide content. The analyzed ratio of sulfide to heavy metals was compared to the ratio which would be predicted if it was assumed that all heavy metals in these solids were precipitated as sulfides. For Test LT-01, the amount of sulfide in the solids proved to be over 75 percent of the predicted amount. For Test LT-02, the amount of sulfide present in the solids was over 97 percent of the predicted amount. This relatively good agreement provides a check both on the analytical procedures and on the assumptions made regarding the stoichiometries of the reactions of the various heavy metals with sodium sulfide.

Lime Treatment Process Balances

The inlet and outlet streams for the lime treatment process were sampled and analyzed during all five tests. These inlet and outlet data allowed element balances to be calculated across the lime treatment process. Also, the lime addition rate to the process was calculated by difference. These data were checked for consistency by the following observations:

1) Element balances were checked for closure.

2) The charge balance in the solid phase of the outlet was checked for an excess of cations. Some of the heavy metal content remaining in the inlet to the lime treatment should have precipitated as hydroxides.

Since hydroxides were not analyzed, an excess of cations in an amount equal to the heavy metals precipitated as hydroxides should have been present.

3) The solids in the outlet were checked to determine the percent accountability. If a low percentage of the solids was accounted for when summing all of the species analyzed (including the estimated magnesium and hydroxide content), then apparently some major species in the solids were not analyzed for or the analyses were in error.

Tables 24 through 28 present the element balances around the lime process for the five tests. The element balances for metals which are present in significant quantities show good agreement in all tests except ST-03 (Table 26). For this test, it appears that the amount of solids collected with the sample was not representative; that it, it appears that some solid-liquid separation occurred as the sample was taken.

The charge balance in the solid phase of the lime process outlet was checked by calculating the number of milliequivalents of each compound in the amount of solids filtered from one liter of sample. Magnesium content was not analyzed for, but was calculated from the drop in liquid-phase concentrations. Two tests, ST-01 and LT-01, showed an excess of anions. In these tests, either the calcium analysis in the solid-phase was too low, or less likely, some major cation was present and not analyzed. For the remainder of the tests where an excess of cations was present, the excess was attributed to metal hydroxides. Then the total analysis plus calculated magnesium and hydroxide values were summed and compared to the total mg/ℓ solids to determine an estimated closure. The results of these calculations are discussed below for each test. A sample calculation for Test ST-02 is presented in Table 29.

- Test ST-01. There was a large excess of anions, and only 523 mg of solids out of 1340 mg/ℓ could be accounted for from individual analyses. Since the apparent lime dosage for this test was quite low, these discrepancies probably indicate that the calcium analysis for the solid-phase is much too low.

- Test ST-02. From the excess of cations in the solid-phase, a hydroxide content of 207 mg/ℓ was deduced. This 207 mg/ℓ plus 58 mg/ℓ of magnesium, when added to the solids analyses, totals 905 mg/ℓ of solids. This is an 85 percent closure when compared to the 1070 mg/ℓ total solids determination.

TABLE 24. ELEMENT BALANCES AROUND LIME PROCESS, TEST ST-01

Element	In, Liquid Phase mg/ℓ	In, Solid Phase mg/ℓ	In, Total In mg/ℓ	Out, Liquid Phase mg/ℓ	Out, Solid Phase mg/ℓ	Total Out mg/ℓ	% Closure
As	146	3.2	149	19.1	37.5	56.6	38
Cu	-	0.64	0.64	-	1.9	1.9	297
Pb	-	1.6	1.6	-	4.4	4.4	275
Cd	-	0.23	0.23	-	0.54	0.54	235
Zn	39	0.73	39.7	-	25.5	25.5	64
Fe	18	0.2	18.2	0.1	17.4	17.5	96
Hg	0.011	0.09	0.10	0.011	0.25	0.26	260
F	89.7	-	89.7	34.4	37.8	72.2	80
Sulfate	1470	-	1470	1250	186	1436	98
Na	1305	-	1305	1280	-	1280	98
Mg	60.0	-	60.0	1.88	NA	-	-
Ca	48.3	.09	48.4	157	15	172	-

NA - Not analyzed

TABLE 25. ELEMENT BALANCES AROUND LIME PROCESS, TEST ST-02

Element	In, Liquid Phase mg/ℓ	In, Solid Phase mg/ℓ	In, Total In mg/ℓ	Out, Liquid Phase mg/ℓ	Out, Solid Phase mg/ℓ	Total Out mg/ℓ	% Closure
As	16.0	-	16.0	1.8	15.0	16.8	105
Cu	-	-	-	-	0.1	0.1	-
Pb	-	-	-	-	0.2	0.2	-
Cd	-	-	-	-	0.1	0.1	-
Zn	16.4	-	16.4	-	22.5	22.5	137
Fe	7.9	-	7.9	0.2	10.3	10.5	133
Hg	0.016	0.016	0.032	0.012	0.03	0.042	131
F	82.3	-	82.3	20.8	51.4	72.2	88
Sulfate	1700	-	1700	1300	125	1425	84
Na	1080	-	1080	1068	-	1068	99
Mg	51.6	-	51.6	0.25	57.8	58.0	113
Ca	49.3	.04	49.3	234	330	564	-

TABLE 26. ELEMENT BALANCE AROUND LIME PROCESS, TEST ST-03

Element	In, Liquid Phase mg/ℓ	In, Solid Phase mg/ℓ	In, Total In mg/ℓ	Out, Liquid Phase mg/ℓ	Out, Solid Phase mg/ℓ	Total Out mg/ℓ	% Closure
As	33.1	-	33.1	4.1	8.7	12.8	39
Cu	-	-	-	-	0.04	0.04	-
Pb	0.2	-	0.2	-	0.05	0.05	25
Cd	-	-	-	-	0.01	0.01	-
Zn	15	-	15	-	5.6	5.6	37
Fe	14.6	-	14.6	-	3.3	3.3	23
Hg	0.044	-	0.044	0.01	-	0.01	23
F	103	-	103	32.9	NA	-	-
Sulfate	1970	-	1970	2150	14.2	2164	110
Na	1217	-	1217	1450	-	1450	119
Mg	67.0	-	67.0	0.50	NA	-	-
Ca	53.8	.03	53.8	312	45	357	-

NA - Not analyzed

TABLE 27. ELEMENT BALANCE AROUND LIME PROCESS, TEST LT-01

Element	In, Liquid Phase mg/ℓ	In, Solid Phase mg/ℓ	Total In mg/ℓ	Out, Liquid Phase mg/ℓ	Out, Solid Phase mg/ℓ	Total Out mg/ℓ	% Closure
As	37.8	--	37.8	1.9	26.7	28.6	76
Cu	--	--	--	--	--	--	--
Pb	--	--	--	--	0.3	0.3	--
Cd	0.03	--	0.03	--	0.03	0.03	100
Zn	22.0	--	22.0	0.3	25.9	26.2	119
Fe	7.2	--	7.2	--	9.2	9.2	128
Hg	0.012	--	0.012	0.008	0.012	0.020	167
F	120	--	120	26.0	78.3	104	87
Sulfate	1640	--	1640	1430	124	1554	95
Na	1125	--	1125	1088	--	1088	97
Mg	62.5	--	62.5	0.9	NA	--	--
Ca	41.3	0.04	41.3	188	11.2	199	--

NA - Not analyzed

TABLE 28. ELEMENT BALANCE AROUND LIME PROCESS, TEST LT-02

Element	In, Liquid Phase mg/ℓ	In, Solid Phase mg/ℓ	Total In, mg/ℓ	Out, Liquid Phase mg/ℓ	Out, Solid Phase mg/ℓ	Total Out mg/ℓ	% Closure
As	24.2	2.1	26.3	1.9	21.6	23.5	89
Cu	-	0.27	0.27	-	0.07	0.07	26
Pb	0.2	1.7	1.9	0.2	0.46	0.66	35
Cd	0.12	0.27	0.39	-	0.07	0.07	19
Zn	13.6	0.54	14.1	-	27	27	191
Fe	14.8	0.08	14.9	-	14.9	14.9	100
Hg	0.008	0.10	0.11	0.012	.03	.04	38
F	86	-	86	26.2	71.6	97.8	114
Sulfate	1670	-	1670	1790	78	1870	112
Na	1163	-	1163	1267	-	1267	109
Mg	65.9	-	65.9	2.1	NA	-	-
Ca	62.5	.15	62.7	247	207	454	-

NA - Not analyzed

TABLE 29. SAMPLE CALCULATION FOR CHARGE BALANCE ON SOLIDS AT LIME TREATMENT PROCESS, TEST ST-02

CATIONS			ANIONS		
	Mg/ℓ of Slurry	Milli-eq/ℓ of Slurry		Mg/ℓ of Slurry	Milli-eq/ℓ of Slurry
As	15.0	0.60	$SO_4^{=}$	125.2	2.61
Cu	0.1	-	$S^{=}$	85.6	5.35
Pb	0.2	-	F^{-}	51.4	2.71
Cd	0.1	-	OH^{-}	(208)*	(12.2)*
Zn	22.5	0.69	Total	470	22.9
Fe	10.3	0.37			
Hg	-	-			
Ca	329.6	16.48			
Mg	57.8	4.76			
Total	436	22.9			

*By Difference

Total Weight Accounted for (mg/ℓ of slurry) = Total Cations + Total Anions
= 436 mg/ℓ + 470 mg/ℓ
= 906 mg/ℓ

Total Weight Solids Reported (mg/ℓ of slurry) = 1070 mg/ℓ

$$\text{Percent Closure on Solids} = \frac{906}{1070} \times 100$$
$$= 85\%$$

- Test ST-03. Due to the apparent solids content error for this test, as discussed above, a corrected solids content was used in this calculation. There is a large excess of cations; however, there is no sulfide analysis for these solids. Fortunately, the molecular weight of one milliequivalent of hydroxide (17 mg) is nearly the same as the molecular weight of one millequivalent of sulfide (32mg/2 or 16 mg). Consequently, little error is introduced by assuming that all of the charge imbalance is attributable to hydroxide. The 173 mg/ℓ of magnesium and 319 mg/ℓ of corrected compound and element analyses results in 559 mg/ℓ being accounted for in the solids. This is 93 percent of the 600 mg/ℓ of corrected solids content. Because of the many assumptions required to make this calculation for this test, this number is probably not significant. However, the high closure calculated does lend some credence to the corrections made.

- Test LT-01. An excess of anions is apparent in the solid-phase analyses. Also, only 443 of 1350 mg/ℓ of solids are accounted for. This combined with the very low calculated lime addition rate for this test probably indicates that the calcium analysis in the solid phase is too low.

- Test LT-02. The excess of cations in the solid phase suggests that 163 mg of hydroxides are present in the solid phase. However, even with this amount of hydroxide, only 51 percent of the 1350 mg/ℓ solids are accounted for. Since the heavy metal balances for this test show reasonably good agreement, this discrepancy is probably indicative of an incorrect, low calcium analysis in the solid phase. This theory is supported by the fact that the apparent CaO dosage of 392 mg/ℓ is somewhat lower than the apparent dosages of over 500 mg/ℓ in Tests ST-02 and ST-03, which showed good solids accountability.

Sulfur Balance Calculations

Sulfur balance calculations were made in an attempt to verify measured sulfide addition rates. A first attempt to verify these rates was to calculate the amount of sulfur leaving the system as $S^{=}$ and to compare this amount to the measured sulfide addition rate. Sulfide leaves the system

with the heavy metals precipitated in the sulfide process, and in both the solid- and liquid-phases leaving the lime treatment process. Other losses occur in the plant ventilation system and through reactions with sulfites. The amount of sulfide leaving the system with heavy metals precipitated in the sulfide process was quantified by assuming that one milli-equivalent of sulfide was precipitated with each milli-equivalent of heavy metal removed. Sulfide leaving the system from the lime treatment process was quantified from the sulfide analyses of both the liquid- and solid-phases. Only one test, LT-02, showed tangible evidence of loss of H_2S to the plant ventilation system. In this test, the outlet of the first reaction tank contained 1.1 mg/ℓ of free sulfide, but by the outlet of the third reaction tank, this free sulfide was down to 0.1 mg/ℓ. Table 30 summarizes the results of this sulfide balance.

TABLE 30. SULFIDE BALANCE

	Milliequivalents of $S^{=}$/per liter				
	Test ST-01	Test ST-02	Test ST-03	Test LT-01	Test LT-02
Sulfide precipitated in process	12.0	5.5	5.6	6.2	6.7
Sulfide in lime treatment outlet‡	8.6	5.4	3.5*	6.6	2.9
Total sulfide accounted for	20.7	10.9	9.1	12.8	9.6
Sulfide addition, best estimate	15.6	13.2	10.4	20.0	24.1

‡ Note that sulfide leaving the system in the lime treatment outlet, which is essentially wasted, is of the same order of magnitude as that consumed in the process itself.

* Estimated, solid-phase sulfide; analysis missing.

Tests ST-01, ST-02, and ST-03 show reasonable agreement between the sulfide added and the sulfide accounted for. For all three of these tests, the amount accounted for is within the range of uncertainty of the sulfide addition rate. For Tests LT-01 and LT-02, however, the agreement between the amount of sulfide added and the amount accounted for is poor, even considering the uncertainty in the sulfide addition rate measurement. In all tests, the sulfide leaving the system in lime treatment process solids represented a large sulfide loss.

Next, a balance of SO_x was attempted. Table 31 summarizes these data. Note that for every test, the sulfate quantity increases, indicating oxidation of sulfite across the system. Also, in every test except Test ST-01, where sulfite in the outlet of the sulfide process was not analyzed, the sulfite quantity drops across the system. Part of this drop is attributable to oxidation to sulfate. However, in the four tests where the data are available, the sulfite quantity decreases in a greater amount than the sulfate quantity increases. This could be an indication that some reaction of excess sulfide with sulfite occurs, forming thiosulfates. As discussed in a footnote to Table 30, thiosulfate can be analyzed for by the iodimetric titration method used by Boliden to determine sulfite concentration. However, four moles of sulfur as thiosulfate react with the same amount of iodine as one mole of sulfur as sulfite. Consequently, some sulfur would appear to have "disappeared" by this iodimetric method if sulfite has been converted to thiosulfate. Unfortunately, there was no sulfite analysis on the outlet stream, for Test ST-01, the one test where there was apparently no excess sulfide added and all sulfide appears to be otherwise accounted for. Consequently, what would have been a check on the observation that thiosulfate may be formed cannot be made.

Sulfur Balance Data

The sulfide balances for the two long runs and the three short runs are not reliable, since the method used for analyzing sulfide in these samples was afterwards found to be inappropriate for this application. In the two special short tests, the results of which are presented in Table 11, the complex reaction between sulfide and sulfur dioxide (sulfite) has been taken into consideration. The analytical methods used for these two tests have, as far as possible, been adapted to the different sulfur compounds present.

Sulfur balance calculations were made based on the results of the two special short tests, SST-01 and SST-02. The sulfur in the two inlet streams and in the sodium sulfide reagent added was compared to the amount of sulfur in the stream leaving the third reaction tank. The results were as follows:

SST-01

Sulfur in inlet streams:	3040 g-moles/hr
Sulfur in sulfide reagent:	1410 g-moles/hr
Total sulfur in	4450 g-moles/hr
Sulfur out of Reaction Tank III:	3300 g-moles/hr

$$\% \text{ Closure} = \frac{3300}{4450} \times 100 = 74\%$$

TABLE 31. SO_x MATERIAL BALANCE ACROSS SULFIDE PROCESS

	Test ST-01	Test ST-02	Test ST-03	Test LT-01	Test LT-02
SO_4 in, milli-eq/ℓ	27.9	33.1	36.3	30.0	29.4
SO_3 in,* milli-eq/ℓ	26.3	19.9	16.4	18.1	14.0
Total SO_x in, milli-eq/ℓ	54.2	53.0	52.7	48.1	43.4
SO_4 out, milli-eq/ℓ	30.6	35.4	41.0	34.2	34.8
SO_3 out,* milli-eq/ℓ	NA	12.7	8.4	12.9	6.9
Total SO_x out, milli-eq/ℓ	--	48.1	49.4	47.1	41.7
Apparent SO_x decrease across system, milli-eq/ℓ	--	4.9	3.3	1.0	1.7

NA - Not analyzed.

*Determined by iodimetric titration, by the reaction:

$$SO_3^{=} + I_2 + H_2O \longrightarrow SO_4^{=} + 2HI$$

where each mole of sulfur consumes one mole of I_2. However, if thiosulfates are present in the outlet stream due to liquid-phase Claus reactions, thiosulfate reacts as follows:

$$2S_2O_3^{=} + I_2 \longrightarrow S_4O_6^{=} + 2I^{-}$$

In this reaction, four moles of sulfur consume one mole of I_2. Consequently, any $SO_3^{=}$ which has been converted to $S_2O_3^{=}$ by reaction with excess sulfide will consume less iodine, appearing to be a decrease in $SO_3^{=}$ concentration beyond that which is converted to $SO_4^{=}$ by natural oxidation.

SST-02

Sulfur in inlet streams:	3615 g-moles/hr
Sulfur in sulfide reagent:	1000 g-moles/hr
Total sulfur in	4615 g-moles/hr
Sulfur out of Reaction Tank III:	5665 g-moles/hr

$$\% \text{ Closure} = \frac{5665}{4615} \times 100 = 123\%.$$

These balances are based on the "total sulfur" analyses in both the solid- and liquid-phase for Sample Points 01 and 02 (inlet) and Point 05 (outlet of Reaction Tank III) in Table 11. In all of the streams except the solid phase, Point 05 on both Tests SST-01 and SST-02, the sums of the individual sulfur species were reasonably close to the "total sulfur" analysis. For the solid-phase at Point 05 for Test SST-02, the sum of the sulfur species was especially low, only about half of the "total sulfur" analysis. If it is assumed that this "total sulfur" analysis is an error and the sum of the solid-phase sulfur species is instead used in the balance above, the sulfur balance for Test SST-02 becomes:

Total sulfur in	4615 g-moles/hr
Sulfur out of Reaction Tank III:	4650 g-moles/hr

$$\% \text{ Closure} = \frac{4650}{4615} \times 100 = 101\% .$$

In light of the fact that Test SST-01 involved "grab" sampling, while Test SST-02 involved compositing samples over a three-hour period, the respective sulfur balance closures of 74 percent and 101 percent (corrected) seem very reasonable.

Sulfite-Sulfide Interaction

Several observations indicated the disappearance of sulfide from solution through a pathway other than heavy metal precipitation:

- No H_2S smell in the solutions, in spite of apparent stoichiometric overdoses and the acidic pH values
- Non-closure of the sulfide balance
- Disappearance of sulfite
- High apparent sulfite and calcium values in the effluent of the fluoride treatment plant.

The calcium sulfite solubility ($CaSO_3 \cdot 1/2\ H_2O$) in neutral water of 18°C is 43 mg/ℓ. The solubility decreases with increasing alkalinity. The analytical results at the exit of the fluoride treatment plant, however, indicate much higher liquid-phase calcium sulfite concentrations.

Solutions containing SO_2 and H_2S are known as Wachenroder's solutions. Hydrogen sulfide and sulfur dioxide react to form thiosulfate, polythionates, and elemental sulfur. The very complex reaction mechanism is shown in Figure 7. Figure 8 shows that the reaction proceeds rapidly and is complete after 4 to 10 minutes. This time compares to a residence time of 30 minutes in each of the reaction tanks and 4 to 6 hours in the thickener.

These reactions explain the absence of an H_2S smell, the non-closure of the sulfide balance, and the disappearance of sulfite.

The high sulfite values in the system reported in Tests ST-01, ST-02, ST-03, LT-01, and LT-02 are apparently caused by thiosulfate interference. Sulfite, thiosulfate, and As^{+++} react with iodine according to the following equations:

Sulfite Iodine Reaction:

$$SO_3^{=} + I_2 + H_2O \rightleftharpoons SO_4^{=} + 2HI$$

Thiosulfate Iodine Reaction:

$$2S_2O_3^{=} + I_2 + 2H^{+} \rightleftharpoons S_4O_6^{=} + 2HI$$

Arsenite Iodine Reaction:

$$AsO_3^{3-} + I_2 + H_2O \rightleftharpoons AsO_4^{3-} + 2HI\ .$$

The iodine consumption by thiosulfate and arsenite must be considered in the calculation of the sulfite concentration. This correction was done in the Special Short Tests (SST-01 and SST-02). The more stable intermediates form in acidic solution. The kinetics of the reaction was published by L. Korosy, et al (4). It is reproduced in Figure 8.

In contrast to calcium sulfite, calcium thiosulfate and calcium polythionates are very soluble.

Analysis for Extractable Organic Priority and Non-Priority Pollutants

As part of the characterization of the Boliden sulfide/lime precipitation process, Radian was to determine the fate of any organic compound in the incoming waters. Three water samples at various points in the process were extracted for their organic content with methylene chloride. Extractable organic compounds in the concentrated extract were analyzed by gas chromatography-mass spectrometry (GC-MS). The methods employed are outlined in the

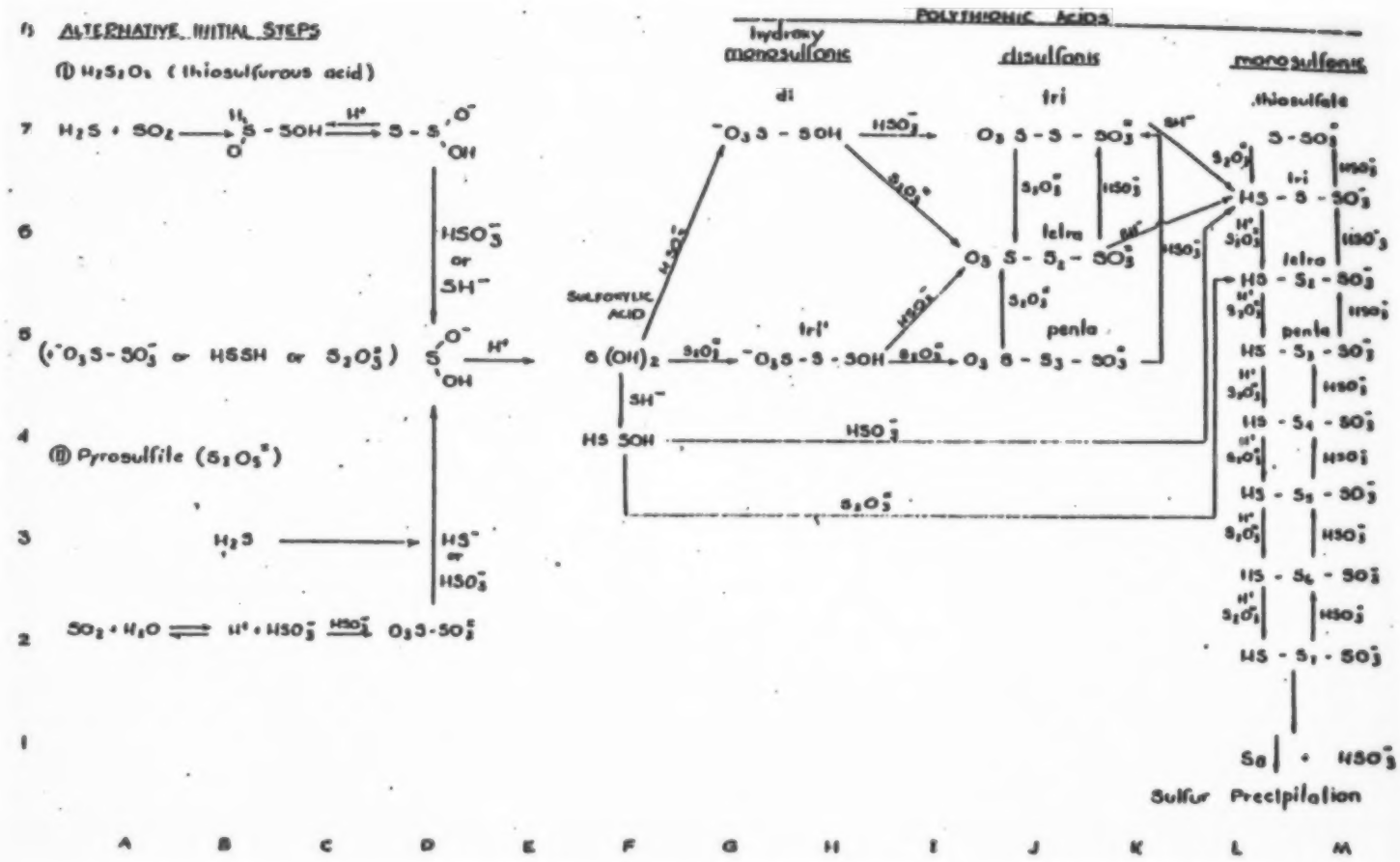

Figure 7. Mechanism for the regeneration of the citrate process (Reference 3).

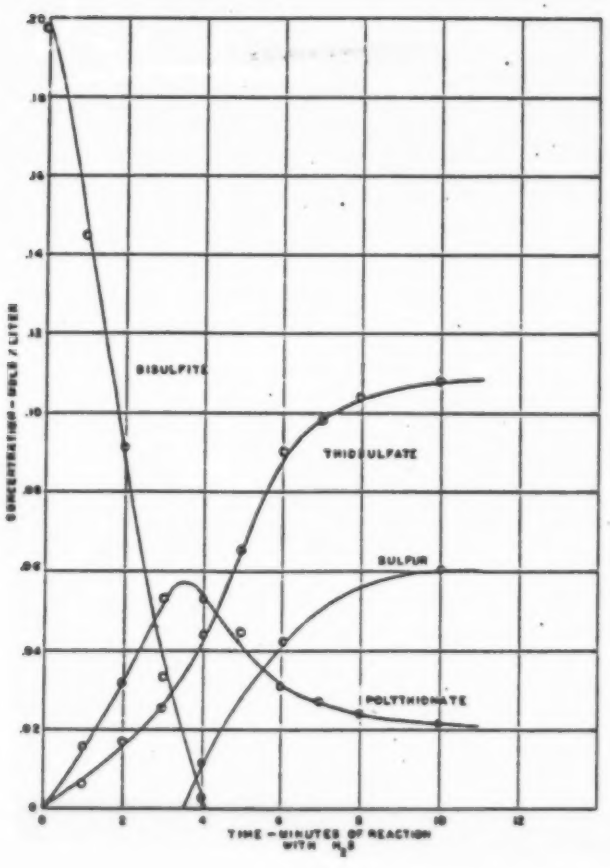

Figure 8. Kinetics of the H_2S - SO_2 interaction (Reference 4).

EPA Protocol, "Sampling and Analysis Procedures for Screening Industrial Effluents for Priority Pollutants", dated April 1977. The organic species which can be quantitatively detected by this procedure are listed in Table 32.

Three water samples were extracted with methylene chloride, according to protocol conditions to give base/neutral and acidic fractions. These samples were taken from a mixed inlet stream to the first sulfide (Sample Points 1 and 2) reaction tank, the multimedia filter outlet (Sample Point 7), and the fluoride treatment tank effluent (Sample Point 8), respectively. These samples represented the inlet and outlet of the sulfide process, and the outlet of the subsequent lime treatment process. Extracted fractions were concentrated down to 1 mℓ each and analyzed using a 2 mℓ injection into a Hewlett-Packard 5985 computer-controlled system. Extracted compounds were identified in each sample by searching the stored mass spectral data.

The results of the GC-MS analyses are summarized in Table 33. Of the organic compounds which would have been identified by this method, only five species were present in detectable quantities. These compounds included dimethyl phthalate, diethyl phthalate, di-n-butyl phthlate, and bis(2 ethylhexyl)phthalates in the base/neutral extract, and phenol in the acid extract. All five compounds were present at the ppb level. The concentrations of these compounds did not appear to vary significantly through the treatment process, indicating that the organic content in the incoming water was unaffected by the process.

TABLE 32. PRIORITY POLLUTANTS

VOLATILE ORGANICS

Acrolein	1,2-Dichloropropane
Acrylonitrile	1,3-Dichloropropene
Benzene	Methylene chloride
Toluene	Methyl chloride
Ethylbenzene	Methyl bromide
Carbon tetrachloride	Bromoform
Chlorobenzene	Dichlorobromomethane
1,2-Dichloroethane	Trichlorofluoromethane
1,1,1-Trichloroethane	Dichlorodifluoromethane
1,1-Dichloroethane	Chlorodibromomethane
1,1-Dichloroethylene	Tetrachloroethylene
1,1,2-Trichloroethane	Trichloroethylene
1,1,2,2-Tetrachloroethane	Vinyl chloride
Chloroethane	1,2-trans-Dichloroethylene
2-Chloroethyl vinyl ether	bis(Chloromethyl) ether
Chloroform	

BASE/NEUTRAL EXTRACTABLE ORGANICS

1,2-Dichlorobenzene	Fluorene
1,3-Dichlorobenzene	Fluoranthene
1,4-Dichlorobenzene	Chrysene
Hexachloroethane	Pyrene
Hexachlorobutadiene	Phenanthrene
Hexachlorobenzene	Anthracene
1,2,4-Trichlorobenzene	Benzo(a)anthracene
bis(2-Chloroethoxy) methane	Benzo(b)fluoranthene
Naphthalene	Benzo(k)fluoranthene
2-Chloronaphthalene	Benzo(a)pyrene
Isophorone	Indeno(1,2,3-c,d)pyrene
Nitrobenzene	Dibenzo(a,h)anthracene
2,4-Dinitrotoluene	Benzo(g,h,i)perylene
2,6-Dinitrotoluene	4-Chlorophenyl phenyl ether
4-Bromophenyl phenyl ether	3,3'-Dichlorobenzidine
bis(2-Ethylhexyl) phthalate	Benzidine
Di-n-octyl phthalate	bis(2-Chloroethyl) ether
Dimethyl phthalate	1,2-Diphenylhydrazine
Diethyl phthalate	Hexachlorocyclopentadiene
Di-n-butyl phthalate	N-Nitrosodiphenylamine
Acenaphthylene	N-Nitrosodimethylamine
Acenaphthene	N-Nitrosodi-n-propylamine
Butyl benzyl phthalate	bis(2-Chloroisopropyl) ether

ACID EXTRACTABLE ORGANICS

Phenol	p-Chloro-m-cresol
2-Nitrophenol	2-Chlorophenol
4-Nitrophenol	2,4-Dichlorophenol
2,4-Dinitrophenol	2,4,6-Trichlorophenol
4,6-Dinitro-o-cresol	2,4-Dimethylphenol
Pentachlorophenol	

PESTICIDES/PCB'S

α-Endosulfan	Heptachlor
β-Endosulfan	Heptachlor epoxide
Endosulfan sulfate	Chlordane
α-BHC	Toxaphene
β-BHC	Aroclor 1016
δ-BHC	Aroclor 1221
γ-BHC	Aroclor 1232
Aldrin	Aroclor 1242
Dieldrin	Aroclor 1248
4,4'-DDE	Aroclor 1254
4,4'-DDD	Aroclor 1260
4,4'-DDT	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
Endrin	
Endrin aldehyde	

METALS

Antimony	Mercury
Arsenic	Nickel
Beryllium	Selenium
Cadmium	Silver
Chromium	Thallium
Copper	Zinc
Lead	

MISCELLANEOUS

Asbestos (fibrous)
Total Cyanides
Total Phenols

*Compounds analyzed for on Boliden water samples

TABLE 33. RESULTS OF GC-MS ANALYSES ON BOLIDEN SULFIDE/LIME PRECIPITATION PROCESS PLANT WATERS

I. Analysis of Base/Neutral Extractables

A. Mixed inlet to Reaction Tank 121, Points 1 and 2

Compound	Concentration (ppb)
Dimethyl phthalate	2.3
Diethyl phthalate	9.2
Di-n-butyl phthalate	5.8
bis(2-Ethylhexyl) phthalate	1.0

B. Outlet, multimedia filter, Point 7

Compound	Concentration (ppb)
Diethyl phthalate	5.7
Di-n-butyl phthalate	4.3
bis(2-Ethylhexyl) phthalate	1.3

C. Fluoride treatment effluent, Point 8

Compound	Concentration (ppb)
Diethyl phthalate	11
Di-n-butyl phthalate	5.6
bis(2-Ethylhexyl) phthalate	1.8

II. Analysis of Acidic Fractions

A. Mixed inlet to Reaction Tank 121, Points 1 and 2

Compound	Concentration (ppb)
Phenol	27

B. Outlet, multimedia filter, Point 7

Compound	Concentration, (ppb)
Phenol	21

C. Fluoride treatment effluent, Point 8

Compound	Concentration (ppb)
Phenol	28

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